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HYDROTHERMAL ALTERATION[1]

GEORGE M. SCHWARTZ

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ABSTRACT

Early in the investigation of epigenetic mineral deposits it was recognized that hot solutions were important and that wall-rocks were commonly highly altered.

Physical changes in the wall-rock are conspicuous, especially bleaching, development of porosity, permeability and textural changes. The changes, however, are varied and some rocks become dark colored, others dense and impervious.

Changes in mineralogy are complex but less commonly only recrystallization may occur. The list of minerals and mineral groups formed by hydrothermal alteration comprises 68 names and doubtless will be expanded as research continues. The most characteristic minerals include sericite, quartz, chlorite, sulfides, epidote, zoisite, clinozoisite, leucoxene, clay minerals, calcite and other carbonates. Minerals formed at an early stage may alter to other minerals as the process continues. Some minerals, such as biotite, may be susceptible to alteration but on occasion form as an alteration product. Quartz is the only abundant primary mineral that commonly resists destruction by hydrothermal processes.

[1] Presidential Address, presented at the Annual Meeting of the Society of Economic Geologists, November 8, 1958.

The chemical composition of rocks and of hydrothermal solutions forms chemical systems of extreme complexity. Therefore, the chemical reactions and ultimate chemical changes are varied. Substances such as water, silica, sulfur, carbon dioxide, potassium, sodium, calcium, magnesium, boron, fluorine, and so on are introduced into the rocks or transferred from one place to another. The composition of the wall-rock exerts a strong influence on the early stage alteration whereas the composition of the solution is dominant in the late stage.

The nature of the process of hydrothermal alteration is such that zones of alteration are a normal result. These are not uniform but naturally depend on the composition of the wall-rock and of the solutions with changes in the solutions during the process having a strong influence.

As a result of intense alteration dissimilar rocks, particularly igneous rocks tend to develop a uniform product consisting in some districts, for example, of quartz and sericite.

A conspicuous feature of the alteration of the wall-rocks of some veins, is that there is little relation to the composition of the vein. Thus gold quartz veins in California have a highly carbonatized wall-rock.

The nature of wall-rock alteration has an important bearing on inferences as to the source of the hydrothermal solutions because of the complex chemical additions in some examples.

INTRODUCTION

THE amount of data that has been published on the subject of hydrothermal alteration and its relation to epigenetic ores is prodigous. Scarcely a description of an epigenetic ore deposit or mineral district published in the past 50 years fails to make some mention of wall-rock alteration. There is, however, a lack of a general discussion of the process and its results. It seemed appropriate, therefore, to attempt a review or summary of the situation as we understand it today. It should be recognized that in thus attempting to generalize, exceptions to almost any statement are bound to exist and complete coverage of ideas is essentially impossible.

The importance of hydrothermal alteration in relation to epigenetic ores was stated by Lindgren (56), as follows: "The study of changes and alterations which the rocks adjoining fissures have undergone is a subject of the highest importance, for in this way a closer insight into the genetic processes of the veins may be obtained." Lindgren (61) later emphasized this importance in his textbooks and his Presidential Address before the Geological Society of America (60).

Hydrothermal alteration is defined in the Glossary of Geology as follows: "These phase changes resulting from the interaction of hydrothermal stage fluids ('hydrothermal solutions') with pre-existing solid phases, such as kaolinization of feldspars, etc. Also used to cover changes in rocks brought about by the addition or removal of materials through the medium of hydrothermal fluids, e.g. silicification."

Hydrothermal alteration is extremely varied and the kind of host rock obviously has a large influence on the result. It is evident, however, that abundant changes in mineralogy, and often in chemical composition, can be made only by relatively large amounts of solutions. The argument that it is unreasonable to assume the large quantities of solutions necessary to form

large ore bodies is not valid because altered rocks are proof that enormous amounts of solutions moved through the rocks quite aside from the ore minerals deposited.

It should be emphasized that in this review hundreds of articles have contributed ideas and only the most pertinent can be cited.

HISTORICAL REVIEW

It seems impossible to trace back to the first recognition of a relationship between hydrothermal alteration and epigenetic mineral deposits. Stutzer (88) states that a manuscript by Carl Martini dated 1819 showed a diagram of a kaolin deposit between iron-bearing veins at the top of a granite stock.

Some realization that ores were related to heated waters and vapors goes back, at least, to Agricola in 1546 but there seems to have been little observation of the wall rocks of veins for a long time. The argument as to whether veins were filled from above or below occupied the few individuals interested in mineral deposits, and veins were almost universally considered to be a result of filling of open spaces.

The theory of lateral secretion developed at an early date and involved leaching of the wall rocks. H. T. De La Beche (30) in 1839 concisely stated the formation of veins by lateral secretion and wrote " . . . or that the liquid contents have acted on the adjoining rocks and dissolved a portion of them."

Darwin (26) in 1846 definitely recognized the relation between metamorphism and metallic veins but just what type of metamorphism he had in mind is not certain except that it was doubtless partly contact action.

Elie de Beaumont (33) in 1847 recognized the importance of mineralizers in ore-bearing solutions of magmatic origin but seems to have paid little attention to their effects on the wall rocks of veins.

Daubree (27) was certainly one of the early workers to recognize that vapors deposited part of their load as impregnations in the surrounding rocks. He wrote extensively on the role of water in the earth's crust and believed that mineral deposition at depth was chiefly a result of hydrothermal effects and that metallic substances were formed by the same causes which produced rock metamorphism. He believed that the waters were of meteoric origin heated by the igneous intrusions. Daubree (28) was not content to summarize and theorize from the work of others but showed experimentally, for example, that cassiterite could be formed by the reaction between perchlorate of tin and water vapor.

Von Cotta (24) stated that ore bearing fluids penetrated the wall-rocks and caused deposits in the rock itself.

Perhaps the earliest detailed description of altered rocks was given by Pumpelly in 1873 (74) and 1878 (75) in his reports on the Michigan copper district. This alteration was regarded by Pumpelly as a result of the circulation of heated meteoric waters.

C. L. Foster published papers in 1876 and 1878 (36, 37) which definitely recognized, described, and illustrated the alteration of granite to greisen and other rocks. Pseudomorphs of cassiterite after feldspar in the wall-rock of

a tin vein was sketched, also other impregnations of the wall rock. Ore was described as occurring in granite without a definite boundary between impregnated granite and the vein.

The publication of Die Lehre von den Lagerstätten der Erde by Albrecht von Groddeck (40) in 1879 marks a sort of milestone because in this general text metasomatic alteration by hydrothermal fluids was emphasized, for example, the alteration of olivine, or augite to serpentine. At Cornwall, doubtless following Foster, he states that pseudomorphs of cassiterite and quartz after feldspar occur in the wall rocks of the veins. Also zinc and manganese minerals were described as alteration products of limestone and dolomite.

One of the earliest detailed descriptions of alteration is given by G. F. Becker in the monograph on the Comstock Lode published in 1882 (10). He evidently was torn between lateral secretion, meteoric waters, and hot solutions but concluded that the solutions must have been hot though of meteoric origin. He states "on the other hand, there is much geological evidence pointing to a deep-seated source of heat probably of volcanic origin."

Posepney's (73) classic paper on the "Genesis of Ore Deposits" published in 1893 gives several illustrations of alteration and impregnation of the country rock drawn from the literature as well as from his own observations. His view is clearly indicated by the following statement "The principal genetic distinction is doubtless between deposits contemporaneous with the country-rock, and those subsequently formed in it." Later on Posepny discusses the process of replacement in some detail (pages 210–212).

The first detailed study accompanied by chemical analyses and thorough microscopic description, thus introducing the style that has persisted to the present, was Lindgren's (55) description of the wall-rock alteration in the gold-silver veins of Ophir, California published in 1894. This was quickly followed by a number of classical studies by Lindgren and shortly by Spurr, Ransome, and in time, by many others. The work since 1900 is too voluminous and well known to require a historical review but references to it will appear throughout this discussion.

PHYSICAL CHANGES

General Statement.—The physical changes in rocks as a result of hydrothermal alteration are extremely varied, and in some respects have not been as thoroughly investigated as chemical and mineralogical changes. Altered rocks are generally more porous and permeable than fresh rocks. This is conspicuously so for the intrusive igneous rocks but there are exceptions for extrusive igneous and for sedimentary rocks. Burbank (18) states that alteration is a result of the penetrative power of solutions rather than diffusion.

Extreme alteration may destroy the coherence of rocks as noted by Weed (93) at Boulder Hot Springs, Montana where granite adjacent to fissures had altered to a loose textured mass. A contrary example is described by Burbank from Bonanza, Colorado where a natural barrier to movement of the solutions was built up by envelopes of siliceous rock.

At Goldfield, Nevada (76) a soft, light-colored aggregate of quartz, kao-

linite, and pyrite is closely associated with ore. Lindgren (58) observed that at Morenci the porphyry was altered to a dull, earthy rock in contrast to the hard compact rocks of the contact zone in limestone.

Silicified rocks, of course, become hard and brittle and Smith (84) notes that tuff in the Silver Standard Mine, resembles felsite and rhyolite.

Color.—Changes in color are common during hydrothermal alteration and are accordingly one of the most useful indications of the process. Because of the abundance of light-colored minerals such as sericite, clay minerals, alunite, quartz, and carbonates the altered rocks are commonly bleached as compared with the unaltered equivalents. Further color change on oxidation of the products of alteration may emphasize the altered zones, for example, by oxidation of pyrite to limonite and hematite.

Limestone in the walls of some of the ore bodies in the Bisbee district were bleached as a result of variable changes in composition notably by the addition of manganese. The bleaching seems mainly a result of the destruction of all carbonaceous matter in the rock regardless of whether or not the chemical composition is much changed.

Bleaching is not necessarily connected with the hydrothermal effects connected with ore deposition. The Bisbee district also furnishes an instructive example. At depth exploration of the limestone east of the productive area revealed a wide bleached zone adjacent to an andesite dike. There is no evidence of mineralization in the area and chemical tests indicated little change in composition of the limestone.

Bleaching is conspicuous in most of the disseminated copper deposits. This is particularly true at Cananea, Mexico where andesite, among other rocks, has been bleached to a very light gray or white color during intense sericitization. Lindgren (57) long ago described conspicuous bleaching in the Idaho basin where biotite and hornblende were bleached or disappeared and feldspar altered to a soft, white, opaque material. Goldfield affords another example of extreme bleaching as does the porphyry in the pit at Morenci, Arizona. Examples are furnished by the bleaching of dark colored igneous rocks such as the broad zone of light gray, sericite rock bordering the veins in the Lava Creek district of Idaho (3), or the extensive bleached zones in argillite of the Coeur d'Alene district. Granodiorite and diabase at Grass Valley are bleached and otherwise changed so much that they lose their identity according to Howe (41).

At the Silver Standard Mine (84) Hazelton, B. C., each vein is enclosed in an alteration zone. Tuff is bleached from gray to a cream or tan color. The tuff also becomes hard and brittle and resembles felsites. Dark green chloritic lavas in the Beattie Mine, Quebec (29) are bleached to a pale greenish yellow color.

Exceptions to bleaching are common such as the dark rocks that resulted from the development of chlorite at Ray, Arizona (81). Chloritic alteration in the Abrigo limestone of the Cole Mine at Bisbee, Arizona formed a dark green, almost black rock. Less argillaceous beds are a grayish green as a result of the development of epidote. In some of the Quebec gold deposits black tourmaline has replaced gray or greenish rocks. Knopf (52) described

a black tourmaline-quartz rock developed in a sericitized granite at Rimini, Montana. In the Metaline district of Washington (70) zinc occurs most abundantly near gray or black jasperoid, a replacement of limestone. In the Northern Empire Mine of Canada (11) the rocks near the veins are brown due principally to introduction of carbonate.

James (46) states that the granodiorite of the Siscoe Mine becomes darker due to the formation of chlorite, epidote, and locally tourmaline. At the Nighthawk Penninsular gold mine Byers (19) found the rock darkened due to the development of light brown ankerite as an alteration product.

Altered rocks frequently have some shade of green color as a result of the alteration to chlorite, epidote, mariposite, and serpentine. At the Chesterfield Mine (14) an emerald-green zone is described. Byers (19) refers to areas of bright green fuchite in the outer zones of alteration in the Nighthawk-Penninsular gold mine.

Rocks with a primary red or pink color commonly lose their color as the iron is sulfidized but Derry (31) has described an example in the Canadian Malartic mine where a "red alteration" is developed by the formation of red feldspar and the removal of biotite which presumably furnished the iron to form hematite that colors the feldspar.

Varied rocks tend to become the same color on alteration but different zones range considerably in color. The rocks at Casapalca, Peru (67), for example, show a sequence of color zones in the wall-rock with white near the vein, followed outward by pink, green and finally purplish in the little-altered rock.

Progressive change at places results in change from a dark gray rock to green as chlorite developed and then grayish white as chlorite was replaced by sericite and carbonate. A good example is described by Finlayson (35) for the Hauraki goldfields in New Zealand. Similarly Anderson (2) described a progressive change along mineralized fault zones in the Clark Fork district from blackish, reddish, or dark green to pale green.

Burbank (17) described five kinds of silicified rocks in the Bonanza Mining district of Colorado. These are white or grayish quartz-chalcedony; reddish, brownish, black "jasper"; white or gray quartz-alunite; quartz-kaolinite; and quartz, kaolinite, sericite.

Texture.—In igneous rocks hydrothermal alteration generally resulted in disseminated grains or a mat of exceedingly fine-grained minerals so that a pronounced decrease in grain size resulted. In carbonate rocks alteration commonly results in recrystallization to coarser grained rocks, but this is not uniformly true. In the Bisbee district replacement of limestone by manganocalcite locally resulted at places, in dense fine-grained rocks, some resembling unglazed porcelain. At Morococha (68) hydrothermal anhydrite is coarser grained near the ore.

Replacement of feldspar phenocrysts by clay minerals, sericite, alunite, etc., results in an extreme change in grain size. For example, at Ray, Arizona (81), feldspar phenocrysts ranging up to 4 centimeters in length are partly replaced by sericite flakes averaging about .01 mm in diameter or a reduction in grain diameter to one-fourth hundredth. Chlorite in the same rocks aver-

age about .04 mm or a reduction to one-one hundredth. Quartz that has replaced carbonate and other rocks is commonly cryptocryptalline—the so-called jasperoid.

Even though fine-grained aggregates replace large grains it is rare to have the original texture completely destroyed. Shadows of phenocrysts remain and the distribution of various mineral species give clues to the original texture. In the porphyries primary quartz in the matrix largely resists replacement and reveals the groundmass texture. Examples have been described, however, where the primary texture is completely destroyed. Anderson (1) found in the wall-rock of the Atlantic district, Idaho that the texture was preserved in the early stages of alteration but was finally obliterated in the intense phase.

Replacement of carbonate rocks because of its completeness, at places, has obliterated all evidence of original textures and structures. This is particularly true of intense replacement by silica and sulfides but is not necessarily true as sulfides may faithfully retain the bedding. The gold deposits in the Deadwood formation of the Black Hills show silicification of dolomite with the preservation of even minute textures and structures; particularly good examples are furnished by flat-pebble conglomerates.

Not all hydrothermally altered rocks appear greatly affected but, on the contrary, may appear fresh on megascopic examination. Porphyry from a dike in limestone of the Bisbee district was collected as an example of fresh porphyry but on microscopic examination proved to consist of about fifty percent calcite, epidote and other secondary minerals.

Dolomitized limestones are generally coarser grained than the fresh rocks and unless the relation to the primary limestone can be recognized may appear entirely unaltered.

Fractures.—Permeability is necessary for a high degree of hydrothermal alteration and in many districts intense fracturing and brecciation is conspicuous. This has been particularly true of the disseminated copper deposits and there have been several suggestions to account for the intensity of fracturing. None of the explanations has found wide acceptance as recently noted by Martin (65), who also emphasized the fact that the intensity of shattering seem to be directly proportional to the alteration and unaltered rocks seem to lack the intense shattering so some genetic relation between fracturing and alteration is implied. Martin suggested a relation between alteration and a loss of competency. Wandke (92) in 1925 evidently had more or less spontaneous minute fracturing in mind as expressed in the title "Brecciation by Replacement."

In his studies of the deposits of La Plata Mountains Eckel (32) concluded that the control in non-calcareous rocks was physical and structural rather than chemical.

MINERAL CHANGES

It is probably accepted that the minerals formed during hydrothermal processes depend on four main factors: (1) Composition of the original minerals and rock, (2) composition of the solution, (3) temperature, and (4)

pressure. A fifth, time, is doubtless of some importance because it is evident that equilibrium is not commonly reached during hydrothermal processes and the stage at which action ceases is therefore important. The number of minerals formed is large and the list has grown rapidly in recent years as more detailed studies by modern technique have been made. A case in point is the group of clay minerals; early in this century about the only clay mineral assigned to a hydrothermal origin was kaolinite and only a few workers recognized it as a hydrothermal mineral. We now know that many clay minerals form in large amounts during hydrothermal processes. It is doubtful if there is a single clay mineral that can be said not to have formed during hydrothermal activity at some time or place.

As would be expected the common primary minerals of rocks show a variety of alteration products, and generally, there is a relation between the composition of the primary mineral and the products derived from it but this is not necessarily so as will be clear from the data presented below. It is also characteristic that minerals formed early in the process of alteration are attacked by the minerals formed later in the process, for example, the replacement of chlorite by sericite or chlorite by epidote or carbonate.

Examination of the literature shows that certain minerals are common alteration products and occur in a majority of descriptions. The ones about which there would be little debate include sericite, quartz, chlorite, sulfides (especially pyrite), epidote, zoisite, clinozoisite, calcite or other carbonates, and leucoxene. The clay group of minerals are abundant in many districts but of little or of no importance in others.

In general feldspars are altered to sericite, clay minerals, alunite and to a minor degree to many other minerals especially carbonate and epidote-zoisite in plagioclase.

Feldspars, (albite, orthoclase, adularia) occur as alteration products, rather abundantly in numerous districts in spite of the fact that primary feldspars are generally extremely altered.

Pyroxenes, amphibole, and biotite commonly alter to chlorite but epidote, carbonate, pyrite, serpentine, and leucoxene are frequent products.

Biotite is normally one of the first minerals to be attacked but less commonly it is an alteration product. Stevenson (87) states that in the Red Rose tungsten mine the diorite wall rock within a foot of the scheelite ore body is completely biotitized and strong sericitization extends for 50 feet beyond the vein.

It is extremely difficult to obtain a complete list of minerals formed by hydrothermal alteration and there is naturally some difference of opinion on certain examples, moreover, new minerals are added to the list as intensive investigations are completed. Following is the list compiled from some hundreds of references.

In a general way quartz, sericite and clay minerals are characteristic of the intermediate and acidic igneous rocks; chlorite, epidote, albite and carbonates of the basic igneous rocks; carbonates and quartz of the limestones and dolomites. Slates and schists are commonly characterized by sericite and dolomite.

The role of some of the more important minerals formed by hydrothermal

TABLE 1

MINERALS FORMED BY HYDROTHERMAL ALTERATION

Actinolite	Magnetite
Albite	Native, copper, gold, silver
Allophane	Manganocalcite
Alunite	Manganosiderite
Anauxite	Mariposite
Anhydrite	Montmorillorite
Ankerite	Muscovite
Antigorite	Nacrite
Apatite	Natroalunite
Barite	Native copper
Beidellite	Nontronite
Biotite	Ottrelite
Calcite	Orthoclase
Cassiterite	Prehnite
Chlorite	Pyrophyllite
Chloritoid	Rhodochrosite
Cinnibar	Quartz (several varieties)
Cordierite	Sericite
Diaspore	Serpentine
Dickite	Siderite
Dolomite	Specularite
Epidote	Spinel
Fluorite	Sphene
Fuchsite	Sulfides (many)
Garnet	Topaz
Gedrite?	Talc
Gypsum	Tourmaline
Halloysite	Tremolite
Hematite	Zunyite
Hornblende (uralite)	Zeolites
Hydromica (illite)	Zoisite & clinozoisite
Kaolinite	Tellurides
Magnesite	

alteration deserves comment. As previously noted silicification may be intense during hydrothermal alteration but where quartz is a lesser constituent of an altered rock its origin may be difficult to determine. Commonly most of the quartz may be primary and retain its form and distribution thus aiding in identifying the nature of the primary rock as was shown by the writer (80) in an example from Colorado. Where hydrothermal effects are severe the primary quartz may recrystallize thus obscuring its origin. Perhaps more important is the amount of silica released by alteration of feldspar to sericite or clay minerals. This is likely to be fine grained and difficult to identify but calculations from chemical analyses in some altered rocks show much more quartz than can be recognized in thin section. This has been found to be a particularly perplexing problem in the alteration at Morenci, Arizona. Finally there is quartz actually introduced by hydrothermal solutions. This may occur as veinlets and is easily recognized but the source may be near or far depending on processes in other wall-rocks. Silicification is particularly common in carbonate rocks resulting in a fine grained chalcedonic type of quartz rock to which Spurr (86) applied the name jasperoid.

One of the early detailed descriptions of intense silicification is given in the classic by Irving (43–45) in describing the gold deposits of the Black Hills.

Dolomite was completely replaced by silica especially where the ore-bearing solutions were confined beneath relatively impervious shale or porphyry. Other districts where silicification of carbonate rocks is extensive, for example, include Gold Hill and Tintic, Utah; Metaline, Washington; Ely, Nevada; and Bisbee, Arizona. Volcanic rocks are extensively silicified at Bonanza, Colorado, and Tonopah, Nevada.

As suggested above the source of silica in hydrothermally altered rocks may be: (1) primary quartz; (2) the breakdown of highly siliceous minerals such as orthoclase or albite; (3) leaching from rocks through which the solutions passed; (4) magmatic or other deep seated sources. It has long been realized that much quartz even in veins may be formed without addition to the total silica in a district but where large scale silicification of carbonate rocks occurs without any known nearby rock source it is most reasonable to assume a deep-seated source, probably magmatic.

Sericite is without doubt, the most characteristic mineral of hydrothermally altered rocks. In igneous rocks it commonly replaces plagioclase in the early stage but as the process continues it replaces the ferromagnesian minerals, commonly with chlorite as an intermediate product. In long continued sericitization quartz is attacked although seldom, if ever, completely replaced. A reasonably complete discussion of the role of sericite is a project in itself (see Bulin, 15).

Chlorite is a common and, at places, an abundant mineral in hydrothermally altered rocks as has been noted throughout this paper. It was commonly formed at an early stage through the alteration of biotite, hornblende, pyroxene, and other minerals. It also developed on a large scale by the introduction of magnesium and ferrous iron in the Jerome, Arizona and Noranda, Quebec districts. Taylor (89) states that chlorite forms a zone up to 70 feet thick beneath the sulfide at the Quemont mine. It occurs at the top of a dome-like structure and at places extends down the flanks for hundreds of feet. The chlorite is green where chalcopyrite predominates and is black adjacent to pyrite.

Chlorite also forms in impure sediments such as the Abrigo limestone of the Bisbee district. In a recent study of the ore-bearing rocks at Ajo, Arizona the writer found chlorite the most abundant alteration product.

Epidote, zoisite and clinozoisite are common in hydrothermally altered rocks but are rarely abundant. In the Michigan copper district intense epidotization of the lavas is commonly accompanied by native copper. Zoisite or clinozoisite occurs in the initial stages of alteration of plagioclase and epidote in biotite in many districts.

Carbonates of all common varieties are important minerals in many hydrothermally altered rocks. Calcite, dolomite, and ankerite are the chief ones. Siderite, manganosiderite, and manganocalcite, are locally abundant. Ankerite is particularly important in the altered rocks associated with gold deposits in California, Alaska, Canada, and doubtless elsewhere. Dolomite occurs in many altered limestones adjacent to ore bodies, particularly of zinc and lead.

Some less common minerals deserve comment. Tourmaline, for example, is characteristic of pegmatites and so called pneumatolytic deposits. It occurs, nevertheless, in deposits that are typically hydrothermal. The ore of the disseminated deposits at Cananea, Mexico is in thoroughly sericitized igneous rocks but small crystals and aggregates of tourmaline are widespread in what is otherwise typical mesothermal alteration.

Knopf (52) in 1913 recognized a tourmaline silver-lead type of ore deposit in which a black tourmaline-quartz rock developed in quartz monzonite that has been profoundly altered by sericitization. Sulfides and tourmaline are regarded by Knopf as contemporaneous.

The ores of the La Plata Mountains are mainly of the epithermal type and according to Eckel (32) silica, sericite, chlorite and halloysite are the most important alteration products but other clay minerals, tourmaline, epidote, and ankerite have been formed, at places.

Tourmaline is, of course, abundant in greisen developed under so-called pneumatolytic conditions but some workers believe that liquid phase is more important than gas phase in such alterations. In any event the deposits in Bolivia have tourmaline in association with kaolinite, chlorite, muscovite, an assemblage characteristic of the mesothermal environment. Both Samoyloff (79) and Turneaure (91) believed that the deposits were formed under moderate conditions and by liquid rather than gaseous solutions.

Tourmaline is abundant in several gold deposits in and near the Bourlemaque batholith of Quebec. Black tourmaline occurs as vein filling and extensive replacement of schist and granodiorite in deposits classed as hypothermal. James (46) states that in the Siscoe Mine tourmaline occurs locally in the vein and wall rock.

Peculiar green micas occur in the hydrothermally altered rocks of several districts and have been described under such names as mariposite and fuchite. These generally occur in altered rocks of sub-silicic or intermediate composition and the presence of chromium has been suggested as responsible for the green color. Examples are the Pinchi Lake Mercury deposit, Chesterfield Mine, Nighthawk-Peninsular Mine of Canada, the Mother Lode district of California.

Serpentine presents a problem in the discussion of hydrothermal alteration because it is believed that it generally forms in ultrabasic rocks by deuteric action. In the Quebec chrysotile deposits there seems little doubt that recrystallization of the massive to the highly fibrous form was a result of hydrothermal solutions. That both massive and fibrous varieties do result from purely hydrothermal action is shown by the asbestos deposits of Arizona where limestone is replaced by massive serpentine and this has recrystallized to cross-fiber veinlets of high quality. (7)

Finally it should be noted that there is often a contrast in the alteration between igneous and carbonate rocks. Spencer (85b) found sericite the abundant alteration product in porphyry at Ely, Nevada, whereas jasperoid is the common product in limestone. The writer has observed a similar contrast in the Bisbee district and there are doubtless many examples.

CHEMICAL CHANGES

The interaction of chemically complex host rocks and hydrothermal solutions results in intricate chemical changes that are extremely difficult to unravel. Some changes are simple, for example, the replacement of limestone by quartz but the silicification of an igneous rock such as a monzonite porphyry is a very different matter.

The determination of exact chemical changes has always presented a difficult and expensive problem. Chemical analyses of fresh and altered rock permit a general comparison but for quantitative results both bulk and powder specific gravity determinations are necessary, moreover, volume changes in place may be important although in the usual case the bulk volume probably does not change appreciably.

Hydrothermal solutions have obviously introduced a variety of substances into altered rocks. Those of most importance include water, silica, sulfur, carbon dioxide, potassium, sodium, calcium, magnesium, boron, fluorine, chlorine, lithium, phosphorus, and the common metals that are deposited mainly as sulfides and oxides. Evidence from the altered rocks, fumeroles and hot springs shows that CO_2, H_2S, H_2SO_4, HCl, HF are important compounds active in hydrothermal solutions on occasion. It is, of course, to be understood that some elements are added to rocks by the hydrothermal solutions whereas others are being removed. Those removed at one place may be added to nearby rocks through which the solutions move. Thus calcium is commonly removed near veins but may be deposited farther away in the zone of marginal alteration. For example, Ransome (76) noted that part of the lime removed in the quartz-alunite-kaolinite zone at Goldfield was deposited as gypsum and as calcite in the propylitic zone.

The complexity of chemical changes makes generalization difficult and definite examples more useful; nevertheless a few general changes may be noted. By the very nature of the process water is generally added during alteration but exceptions such as intense silicification occur in which water is not added and, if present, may be eliminated.

Potassium is commonly added mainly in the alteration of igneous and metamorphic rocks but it is removed in examples of argillic alteration. At Cripple Creek, Colorado (59) a fresh latite phonolite contained 5.83 percent K_2O whereas the altered equivalent has 13.36 percent. In contrast, at Bonanza, Colorado (17) a fresh andesite contained 4.95 percent K_2O as compared to .27 percent in a silicified andesite. At Cerro de Pasco (39) the amount of alkali added to the sericite zone exceeds that removed from the inner zone of alteration.

Sodium is largely eliminated in most examples of the alteration of igneous rocks but in a few districts albitization has been important, as in the altered diorite of the Treadwell Mine (85a) where soda increased from 5.69 to 10.01 percent. An average of 19 hydrothermally altered igneous rocks compiled from the literature showed only .20 percent soda.

Lime shows changes somewhat analagous to soda, that is, in igneous rocks it is generally lost but carbonation such as occurred in some of the gold-bear-

ing districts of California resulted in a large gain in lime. In limestones the general situation is a decrease in lime and an increase of such substances as silica, magnesium, iron, and manganese.

Magnesia is generally lost in the alteration of igneous rocks but may increase in examples of chloritization. Reber (77) cites the case at the United Verde Mine where quartz porphyry was replaced by chlorite with an increase of MgO from 1.48 to 18.16 percent. Limestone has been dolomitized in many districts with a corresponding increase in magnesia. Recrystallization effected by hydrothermal solutions may alter the grain size and otherwise change limestone and dolomite near ore bodies without much change in the chemical composition but in bleached and recrystallized limestone at Bisbee, Arizona as much as 12 percent manganese has been added to form manganocalcite.

McKinstry (66) has recently pointed out that the iron content of hydrothermally altered rocks is often little changed from that in the fresh rock but in some examples large amounts of iron must be introduced to form rocks with a large content of pyrite, iron-bearing carbonates and silicates.

Carbon dioxide furnishes a particular clear-cut example of addition to hydrothermally altered igneous rocks because it is present in negligible amounts in fresh rocks but forms relatively large amounts in the altered rocks of some mining districts. At Grass Valley, California, carbonatized diabase contains 18.91 percent CO_2 (56).

Quantitative data on the many other elements or compounds involved in hydrothermal alteration are sparse but it is evident that large amounts of fluorine has been added to greisens and to the wall rocks of veins where fluorite is either a gangue or commercial mineral. Bastin (5) cites replacement ore in limestone of the Illinois district that contains 45 percent fluorine.

In some of the gold deposits of Quebec and Ontario tourmaline is abundant and could have formed only by introduction of significant amounts of boron as analyzed tourmalines commonly show between nine and ten percent B_2O_3.

In replacement and disseminated ores large amounts of copper, lead, zinc, molybdenum, arsenic, antimony, gold, silver and other metals have been added to rocks that contained little or none prior to alteration.

The strong control by the composition and temperature of the hydrothermal solution is indicated by examples of a hydrothermal mineral replacing several minerals without much regard to their composition. Sericite forms in plagioclase and ferromagnesian minerals prior to orthoclase showing that availability of potash was not a controlling factor, in fact, it seems evident that orthoclase was relatively stable in the presence of a solution containing potassium.

ZONES OR STAGES

The significance of zones, stages or sequence of alteration is a complex one and has been discussed at length by various writers from different points of view. For the present purpose it will suffice to be concerned primarily with actual zones or stages as described for several districts. There is some consistency in zones but many variations, as would be expected, because of

differences in temperature, pressure, and composition of rocks and hydrothermal solutions.

The zones or stages are by no means uniform in sequence or time of formation and zoning is most clearly shown where more or less isolated veins are bordered by symmetrical zones. The detailed work on the zones at Butte (78) has made that example most widely known but there are others and a few are tabulated below. These are conspicuous examples but it is recognized that at least some zoning is inherent in the process of hydrothermal alteration. Thus ore bodies in limestone are commonly bordered by dolomite, as at Metaline, Idaho, and Goodsprings, Nevada. In the Leadville district manganosiderite bordered many ore bodies and at Bisbee manganocalcite fills the same role. It is normal for epigenetic ores to be bordered by altered rock that fades into unaltered rock away from the ore.

Examples of Hydrothermal Zones

Alleghany, California. Cooke (23).
- Alteration zones in serpentinite
  - Gold-quartz vein
    - Mariposite—20 feet in width
    - Talc—40 feet in width
    - Carbonate—several hundred feet

Boulder County, Colorado. Lovering (63).
- Vein
- Subzone of intense alteration characterized by dickite
- Transition subzone characterized by beidellite
- Outer subzone. Allophane, montmorillonite (?) hydrous mica and sericite
- Unaltered granite

Butte, Montana. Sales and Meyer (78).
- Fracture and vein
- Silicified zone
- Sericitized zone
- Argillized zone
  - Kaolinite and subzone
  - Montmorillonite subzone

Casapalca, Peru. McKinstry and Noble (67).
- Vein
  1. White granular pyritized wall rock, 1–30 feet
  2. Pink, granular with some epidote, 0–30 feet
  3. Green, epidotized with some pyrite, 0–30 feet
  4. Purple, little altered

Castle Dome Mine, and Copper Cities Deposit, Globe-Miami district, Arizona. Peterson (71, 72).
- High pyrite rock
- Quartz, sericite phase
- Clay phase
- Weak prophylitic phase

Cerro de Pasco, Peru. Graton and Bodich (39).
- Vein. Pyrite, enargite, etc.
- Intense zone. Sericite destroyed. Alunite, dickite, zunyite
- Moderate zone. Sericite, pyrite, quartz
- Feeble zone. Chlorite, muscovite, sericite, epidote, calcite
- Unaltered rock

Chuquicamata, Chile. Lopez (62).
Zones or phases of alteration
1. Fresh granodiorite
2. Transition. Chlorite, albite
3. Chiqui porphyry. Albite, sericite
4. Flooded rock. Sericite, quartz
5. Sericitic rock. Sericite plus quartz veinlets
6. Siliceous rock. Quartz
7. Sericitic rock
West Fissure
Iron King Mine, Arizona. Creasey (25).
Vein. Sulfides
1. Most intense. Quartz, pyrite, ankerite
2. Less intense. Same minerals
3. Sericite rock
Leadville, Colorado. Emmons et al. (34).
Fissure
1. Silicified wall-rock
2. Quartz, sericite, pyrite
3. Chlorite, epidote, sericite, calcite
Fresh granite and porphyry
Night Hawk-Peninsular Mine, Ontario. Byers (19).
Ore. Gold plus chalcopyrite, sphalerite, petzite, etc.
Carbonate zone. Ankerite, calcite, pyrite, sericite, quartz, etc.
Fuchsite zone. Fuchsite plus above minerals especially sericite
Chlorite zone
Fresh albite syenite
Oruro, Bolivia. Chase (20).
Vein
Intense phase. Sericite, pyrite, some alunite and tourmaline.
Texture destroyed
Moderate phase. Sericite and pyrite. Texture preserved
Widespread phase. Some sericite, local chlorite
Unaltered
San Manuel, Arizona. Schwartz (82).
Alteration types.
1. Kaolinite-alunite alteration. Most intense
2. Hydromica-pyrite alteration
3. Sericite-pyrite-chalcopyrite alteration. Probably cuts other 3
4. Marginal biotite alteration
No fresh rocks exposed
Santa Rita, New Mexico. Kerr et al. (51).
Stage 1. Comparatively unaltered granodiorite
Stage 2. Incipient alteration. Dull and cloudy feldspar, chloritized biotite
Stage 3. Hydromica-argillic alteration
Stage 4. Silicification and sericitization. Sericite, quartz, alunite
Stage 3 rock is most widespread and contains most of the ore
Telluide, Colorado. Hurst (42).
Vein
Sericite zone—sericite, quartz, pyrite
Propylitic zone—chlorite, calcite, pyrite, etc.
Somewhat altered volcanic rocks
Wallapai District, Arizona. Thomas (90).
Vein
Intense stage. Sericite, clay mineral, sphene
Second stage. Quartz, sericite
Propylitic stage. Chlorite, pyrite, epidote, sericite, clay, etc.
Various fresh rocks

Yellowknife, Canada. Boyle (13).
Vein
Inner zone. Carbonate and sericite
Outer zone. Chlorite and carbonate
Fresh rock. Chlorite schist
Grass Valley, California. Johnston (47–48).
The sequence is as follows:
1. Sericite and carbonates replace feldspar, chlorite replaces hornblende and pyrite all minerals present
2. Sericite replaced carbonates and chlorite
3. Sericite replaced quartz
Cochiti District, New Mexico. Bundy (16).
Zones
1. Prophylitic zone
2. Argillic zone
3. Silicified zone
Fissure vein

The above tabulation and also many other less well defined examples show that no single sequence can be given but there are general tendencies. There are many examples of quartz and sericite near the vein or center of mineralization grading outward to clay minerals, followed by a weak prophylitic zone. At Cerro de Pasco (39), however, clay minerals are characteristic of the intense zone and the same is true of the San Manuel district (82).

In diorite, syenite, serpentine, greenstone and related rocks a carbonate type of alteration is characteristic and fades out to a chloritic or more complex marginal type of alteration.

CONVERGENCE

The writer has previously emphasized that hydrothermal alteration in many cases caused dissimilar rocks to converge to a uniform type, a fact that has been noted by several investigators. Becker (10) evidently had something of the sort in mind when he stated that propylites owe their distinctive characteristics to a common type of alteration. The original rocks altered to propylite in the Comstock Lode area include diorite, diorite porphyry, hornblende-andesite and augite-andesite.

An outstanding example is the Mother Lode (53) where slate, graywacke, quartzite, conglomerate, amphibolite schist, chlorite schist, talc schist and serpentine were all converted to a rock with a large content of ankerite.

At Larder Lake, Cooke (22) states that there are all gradations from basalt, black slate, graywacke, conglomerate, and diorite porphyry to carbonate rocks.

At Casapalca, Peru (67), red beds, tuffs and porphyries become indistinguishable except under the microscope as a result of silicification and sericitization.

In the Waite-Amulet area (94) rhyolite, rhyolite breccia, andesite lavas, andesite and diorite dikes were converted to a cordierite, gedrite and spinel-bearing rock, the so-called dalmatianite.

The alteration of quartz monzonite, alaskite, and two varieties of dacite to an ultimate quartz-sericite mass replacement at the Silver Bell Mine, Arizona, was emphasized by Kerr (50).

Bundy (16) states that in the Cochita district, New Mexico, andesite porphyry and monzonite have a similar alteration product and rhyolite when intensely altered forms clay minerals and resembles the altered basic rocks.

Convergence does not seem to be characteristic of any particular type of alteration but as emphasized by Thomas (90) the development of a single variety of altered rock depends on the composition of the solution and not on the composition of the wall rock. He cites the conversion of diabase, granite porphyry, and hornblende schist to a similar rock consisting of sericite, clay minerals and sphene. This is not to claim that wall-rock is unimportant in hydrothermal alteration because obviously in the early stages the composition of the wall-rock to a considerable extent determined the alteration products but as alteration proceeds to the intense stage the original nature of the rock becomes less and less important.

The extreme to which the process may go is shown by the silicified rocks in which the gold deposits occur in the Deadwood formation. For the most part the silicification attacked the dolomitic beds but where the action was most intense sandstone and shale became jasperoid scarcely distinguishable from the silicified dolomite except for the primary sedimentary structures.

CONTRAST OF VEIN AND ALTERATION PRODUCTS

It is noteworthy that there is commonly a striking contrast in the minerals of veins, presumably vein fillings, and the metasomatic minerals in the wall rocks. Lindgren (56) noted that the wall-rocks of some California gold-quartz veins were highly carbonatized, rather than silicified.

Bastin and Hill (6) stated that in the deposits of Gilpin County, Colorado, the minerals in the fissures were generally different from those formed by replacement of the wall rock in spite of having formed contemporaneously. Some of the distinctive features were the presence of galena and sphalerite in the veins but absent in the wall-rock. Pyrite, on the contrary, was abundant in the wall-rock. Sericite a characteristic alteration mineral is absent in the vein filling.

J. D. Bateman (9) refers to a notable lack of silicification even in inclusions of wall-rocks in the quartz veins of the Uchi gold area of Canada. The wall-rocks are extensively replaced by carbonate (calcite and ankerite), sericite, pyrite, pyrrhotite, biotite and albite.

NATURE AND ORIGIN OF HYDROTHERMAL SOLUTIONS

So much has been written regarding the nature and origin of ore-forming solutions and there is such a diversity of opinion that not much can be added in the available space. The chapter in the Lindgren Volume and Graton's (38) later discussion alone comprise 256 pages.

It has been thought by many that the ore-forming solutions, which means, in many examples, the solutions that cause hydrothermal alteration, were mainly derived from magmatic sources. It seems likely, however, that meteoric or connate water may constitute a considerable part of the solutions whose work we actually observe. Indeed, there are a number who deny a magmatic

origin of solutions and the source of the metals in ores is assigned to deep-seated metamorphism or source beds close at hand. It is improbable that we shall ever be certain of the source of the solutions and metals but it appears to me that the close association of igneous activity, hydrothermal alteration, and ore deposition in such districts as Bisbee, Bingham, Ely, Morenci, Leadville and a host of others is so direct that to deny their relationship is to deny the obvious. Any attempt to explain the source of the ore minerals must also include the source of all the elements introduced into the hydrothermally altered rocks.

Relating the source of lead and zinc, for example, to a source bed while neglecting the large amounts of such elements as magnesium, iron, manganese, potassium, and others, which may accompany the ore forming process is not realistic. In many districts there is a complete lack of evidence that the hydrothermal solutions have gathered the bulk of their load from adjacent rocks either igneous or sedimentary. Whatever the source it is deep seated and beyond observation. This is essentially what Bateman (8) wrote regarding the deposits at Slocan, British Columbia where the metals were not exhaled directly from the granodiorite but came from the unconsolidated interior of the batholith or from the same source that supplied the igneous rock.

Granitization has been shown to be an important process in altering schists to gneisses and, perhaps in extreme cases, gneisses to granite, but it is a significant fact that some examples of granitization are conspicuously barren of ore deposits. On the contrary, rocks that are altered under much less intense conditions resulting in conspicuously hydrous minerals are so extensively associated with ore deposits, particularly of the mesothermal and epithermal classes, that the relation is one of the most constant in the realm of economic geology.

One of the objections to the hydrothermal source of many ore deposits has been the very large amounts of aqueous solutions required to transport large amounts of metal. The answer seems to be that whether we find it difficult to imagine or not, the fact is that enormous amounts of water have been added to the hydrothermally altered rocks so commonly associated with epigenetic ores, particularly those classes as epithermal and mesothermal.

The main part of the Utah copper stock to a depth of 5,000 feet has had, at least, one percent of water added during hydrothermal alteration. This calculates to an estimate of over four million tons. A similar rough calculation for the stock at Morenci, which has more combined water because of the clay minerals, indicates eleven million tons of water.

Liquid inclusions in vein minerals contain some of the substances introduced into rocks during hydrothermal alteration as well shown by Newhouse (69).

There is no necessity of assigning a single source for the elements in hydrothermal solutions. They could not move through large volumes of rocks without modification and there is abundant evidence of the movement of certain elements outward from the centers of intense activity or from the walls of veins.

RELATION OF ORE TO HYDROTHERMAL ALTERATION

Ore deposits of the varieties usually classed as hypothermal to epithermal almost without exception occur in rocks that have been altered to varying degrees. In an extensive review of the literature on ore deposits examples have been sought where important ore deposits occurred with essentially no alteration of the host rock. It is possible that in the peripheral zones of some districts ore may occur with very little if any alteration. The Ruby Mine at Weston Pass at the extreme south edge of the Leadville district is recalled as a probable example. Also the old Galena district in the Black Hills, South Dakota, where rich lead-silver ore occurred in limestone that seems unaltered although detailed studies have not been made. Lovering (64) stated that the Eureka Lily Mine occurs in completely unaltered limestone. It is also true that hydrothermally altered rocks do not necessarily have associated ore.

An attempt was made in the 50th Anniversary volume of ECONOMIC GEOLOGY under the title of "Alteration as a guide to ore" to summarize the relation of ore to altered rocks (83). Different minerals or varieties of alteration are most closely related to ore in different districts. A good example is furnished by chlorite. In most districts chlorite occurs mainly in the marginal alteration zone but in a few districts as brought out in the discussion of mineralogy above at Jerome, Noranda, and to a lesser degree at Ajo, copper sulfides are closely related to chloritization.

In general an area of intense alteration is a good place to prospect for ore. More specifically in developed mines and districts it is necessary to recognize the relation between ore and the local varieties of alteration. For example, in limestones ore may be related to silicified rocks, dolomite, manganosiderite, manganocalcite or perhaps to simply recrystallized limestone. In igneous rocks of intermediate composition sericite is a particularly characteristic alteration product with ore closely related to areas of intense sericitization. In some districts certain varieties of alteration are widespread and not indicative of the localization of ore within the district whereas another variety may be closely related to actual ore occurrence.

Some examples of relations are instructive. In the Siscoe Mine James (46) states that where the vein is bordered by a zone of alteration gold occurs in the vein. At Grass Valley, California (41), the country rock is comparatively fresh near tight, barren veins in contrast to the intense alteration for the productive part of the veins. Bain (4) stated that at Kirkland Lake the amount of replacement of the wall rock especially by chlorite is proportional to the gold content of the adjacent lode. At the Beattie Mine, Quebec (29), the amount of gold and sulfides is generally proportional to the degree of alteration. At Cerro de Passo (39) alunite and dickite never persist far beyond good copper ore. In the Clark Fork district, Idaho (2), the alteration reflects more or less directly the intensity of mineralization.

At Butte Sales and Meyer (78) have shown that the width of the altered zone is proportional to the width of the vein. In the Matachewan district of Ontario (21) the width of the altered zone is proportional to the size of the vein and calcite increases as the vein is approached until it comprises as much

as 50 percent of the vein. In the Quiruvilca district of Peru, Lewis (54) found intense propylitic and argillic alteration as the vein is approached and near the veins and faults the rock is almost completely argillized. Many other examples of a close relation of alteration and ore are cited in the writer's paper noted above. Bischof (12) stated the case in 1866 as follows: "As we find ores in veins, proportionate in quantity to the alteration of the country rock, what other relation can be thought to exist between the two facts than that the abundance of the ore is a result of this alteration."

RELATION OF SUPERGENE ENRICHMENT TO HYDROTHERMAL ALTERATION

Very little has been written regarding the relation between hydrothermal alteration and supergene enrichment. Consideration of the facts, however, leads to the conclusion that hydrothermal alteration and associated processes have had an important effect on preparation of the rock for enrichment by development of porosity and permeability in addition to introducing the necessary primary sulfides. Lindgren (58) long ago described the porous, earthy nature of the altered porphyry at Morenci in contrast to the hard, compact rocks of the contact zone. That same altered porphyry is now the locus of the great open pit copper mine at Morenci.

Examination of the shape of almost any supergene copper sulfide zone shows a close relation to intensity of fracturing and other permeable zones. This is particularly striking in the lower limit of the enriched zone.

AGE OF THE HYDROTHERMAL ALTERATION

New techniques will contribute much to clarify the problems involved in hydrothermal alteration. Through the courtesy of Professors Goldich and Nier the age of biotite in the hydrothermal alteration accompanying ore has been determined for the Ely, Nevada, and Chino, New Mexico districts (Table 2).

The data indicate an age of about 60 million years for the Chino mineralized rock and 120 million years for the secondary brown mica associated with the mineralized rock at Kimberly in the Ely district. In both cases it is believed that the figures reported are the ages of mineralization. The next step is to determine the age of the unaltered intrusive rocks. It is evident that application of modern methods of age determination will do much to clarify the relations between igneous rocks, hydrothermal alteration and ore deposition.

TABLE 2

+ A^{40}/K^{40} AGES ON BIOTITE FROM COPPER DISTRICTS

District	% K	A^{40} cc. (STP)/gm.	A^{40}/K^{40}	Age (mg.)
Chino, New Mex.	6.77	0.0174×10^{-2}	0.00376	63
Ely, Nevada	6.94	0.00348×10^{-1}	0.00733	121

Constants: $= 0.583 \times 10^{-10}$/yr; $= 4.72 \times 10^{-10}$/yr.

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SOME APPLICATIONS OF THERMOCHEMICAL DATA TO PROBLEMS OF ORE DEPOSITS. I. STABILITY RELATIONS AMONG THE OXIDES, SULFIDES, SULFATES AND CARBONATES OF ORE AND GANGUE METALS

HEINRICH D. HOLLAND

ABSTRACT

The problem of mineral association and mineral paragenesis in ore deposits has been the subject of much discussion. The attempts at a rational explanation have, however, been largely unsuccessful since they were not based on sound physical-chemical principles. A new attempt is made in this paper and it is shown that the temperature and the fugacity (f) of oxygen, sulfur and carbon dioxide in ore forming fluids at the time of deposition of the vein minerals largely control the mineralogy of ore deposits. f_{S_2}–f_{O_2}–T diagrams showing the stability fields of sulfides, oxides and sulfates of 19 metals are developed as well as f_{S_2}–f_{O_2}–f_{CO_2} diagrams showing the stability of these compounds and of carbonates of the respective elements. The diagrams are based on recent compilations of thermochemical data; they are used in the second paper of this series to define the approximate composition of ore-forming fluids and the relationships between temperature, pressure, and mineralogy in hydrothermal ore deposits.

INTRODUCTION

THE application of thermodynamic concepts and data to problems in igneous and metamorphic geology is now generally accepted. However in the field of economic geology instances of the applications of thermodynamics are not numerous. Goldschmidt (4) pointed out the relationships between the magnitude of the free energy of formation of the oxides, sulfides, sulfates and carbonates of various elements and their mode of occurrence in nature. Kordes (8) suggested the use of sulfur pressure above sulfides at various temperatures as an aid in understanding mineral assemblages in ore deposits. Recently Sullivan (17) has attempted to correlate, among other properties, the heat and free energy of formation at 25° C of various oxides and sulfides with their occurrence in ore deposits. All of these attempts have serious shortcomings. Goldschmidt's contribution is fundamental but it is too general to be of direct value in economic geology, since the effect of variations in the fugacity of the volatile components was not considered. Kordes confuses dissociation pressure with solubility, and Sullivan carries the problem no further than Goldschmidt while confusing the issue by suggesting that properties such as the heat of formation, the melting point, and the hardness of minerals have a direct relationship with their occurrence in nature.

In recent years a start has been made in Russia toward an understanding

of mineral associations in terms of the pressure of volatiles at the time of ore deposition (1). However, the treatment is not rigorous and has not led to quantitative results.

A completely rigorous approach is that used by Wager and Bartholomé (18) who interpret the mineralogy and textures observed in sulfide blebs of the Skaergaard intrusion of Greenland in terms of relations in the Cu–Fe–S–O phase diagram. This work suffers somewhat from the incomplete state of knowledge as regards this system. Krauskopf (8a) in a recent paper has used some of the same arguments as those presented here.

In this series of papers an attempt is made to apply thermochemical data on oxides, sulfides, sulfates and carbonates to outline the stability fields of the major ore and gangue minerals of ore deposits. From this study it becomes apparent that the mineral assemblages of most ore deposits are thermodynamically stable at the time of formation, that the position of the fields of stability of ore assemblages shift gradually with changing temperature, and that this change can be interpreted in terms of the cooling of gas mixtures in the carbon–oxygen–sulfur–hydrogen system. This first paper will deal with the pertinent thermodynamic relations, with the data used in the calculations and with the development of the diagrams based on them.

SOME THERMODYNAMIC RELATIONS

The problem to be solved first is that of outlining the stability field of common ore and gangue minerals. The principles used in this paper are few in number and are illustrated well in the problem of defining the stability field of native iron and of the oxides of iron. Iron has been chosen for this purpose because a large amount of work has been done on the iron–oxygen system (10), and because the system shows all of the complexities encountered in metal-oxide systems.

The observed relationships are shown in Figure 1. At point 1 native iron alone is stable. If the oxygen pressure is increased, the boundary of the stability field of wüstite, FeO, is reached at point 2, where iron and FeO are in equilibrium. Between points 2 and 3 only wüstite is stable. At point 3 wüstite is in equilibrium with magnetite. If the oxygen pressure is raised slightly, wüstite becomes unstable. Between points 3 and 4 magnetite is the stable iron oxide. At point 4 magnetite and hematite are in equilibrium, and at higher oxygen pressures than that of point 4, hematite is the stable oxide.

A similar sequence is observed if, instead of raising the oxygen pressure, we lower the temperature. Native iron is stable until point 5 is reached. There native iron is in equilibrium with magnetite, since below 550° C wüstite is unstable with respect to iron and magnetite. Between points 5 and 6 magnetite is the stable iron oxide. At point 6 magnetite is in equilibrium with hematite, and at temperatures lower than that of point 6 hematite is the stable iron oxide.

Since iron and oxygen are the only elements present in these compounds, the presence or absence of other elements in the system should be immaterial. However, if other elements are present which enter the structure of

the solid phases (for example titanium in magnetite), the boundary of the stability fields are usually shifted. As has been shown by Sahama and Torgeson (16), effects due to such substitution are normally small.

The presence of other volatiles may change the effective pressure of oxygen in a given system; this will occur when the mixture of volatiles deviates in its behavior from that of a perfect gas. Such deviations are to be expected, particularly in mixtures of polar molecules at high vapor densities. In this treatment I will therefore use the fugacities f, of volatiles rather than their pressure. The fugacity may be thought of as an idealized pressure which measures the escaping tendency of the gas. To visualise this function, we will consider a box containing an iron oxide in contact with a mixture of gases at high temperature and pressure. Let a membrane be fixed on one side of this box, and let this membrane have the property that only oxygen can penetrate through it. If one attaches a manometer to a container attached to the membrane, one will measure the pressure of pure oxygen in equilibrium with oxygen in the gas mixture. The measured pressure will then be the fugacity, provided the pressure is small. When the fugacity of water vapor or other gases present at large pressures are measured, the pressure of the pure gas will still not quite be equal to the fugacity because of non-ideal behavior of pure gases at high pressure.

An alternative way of plotting the data for systems such as the iron–oxygen system is that shown in Figure 1a. Here the function 2.303 RT log f_{O_2} rather than log f_{O_2} has been plotted along the y-axis as in the previous figure. The boundaries of the mineral stability fields are seen to be essentially straight lines in this type of diagram. That such boundaries are straight lines, or nearly so, in many other metal-gas systems as well, has been shown in the compilations by Richardson and his coworkers (11–13). They have shown that for many oxide systems

$$A + CT = 2.303\ RT \log f_{O_2} \tag{1}$$

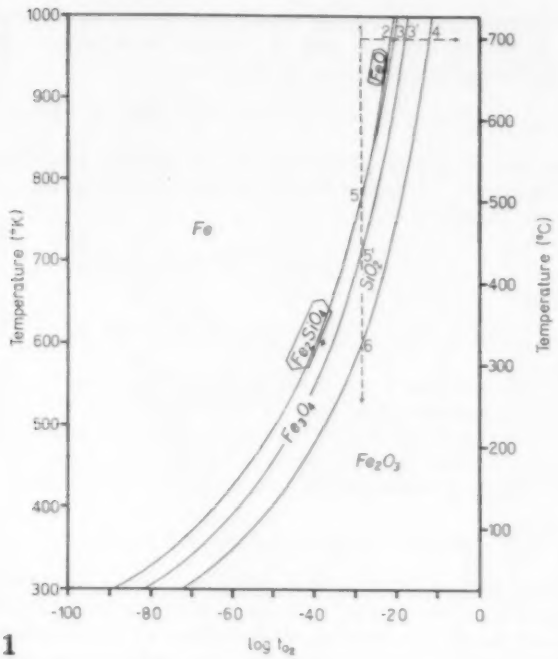
over a considerable range of temperature. The terms A and C are related simply to standard thermodynamic functions of the substances involved (see for instance Rossini (15)). For, consider the reaction

$$2[Fe_3O_4] + \tfrac{1}{2}(O_2) \rightarrow 3[Fe_2O_3], \tag{2}$$

where $2[Fe_3O_4]$ represents 2 mols of pure magnetite in the solid state, $\frac{1}{2}(O_2)$ one half mol of oxygen in the gaseous state, and $3[Fe_2O_3]$ 3 mols of pure hematite in the solid state. The free energy change for this reaction at 298° K can be calculated from the entropy and heat of formation of the substances concerned. These are listed by Kubaschewski and Evans (9) and Rossini et al. (15) and are reproduced in Table 1.

TABLE 1

Substance	ΔH_{298} (Kcal)	ΔS_{298} cal/deg
$2[Fe_3O_4]$	-536.0 ± 2.0	70.0 ± 1.2
$\frac{1}{2}(O_2)$	0	24.51 ± 0.01
$3[Fe_2O_3]$	-591.0 ± 2.1	64.5 ± 1.5



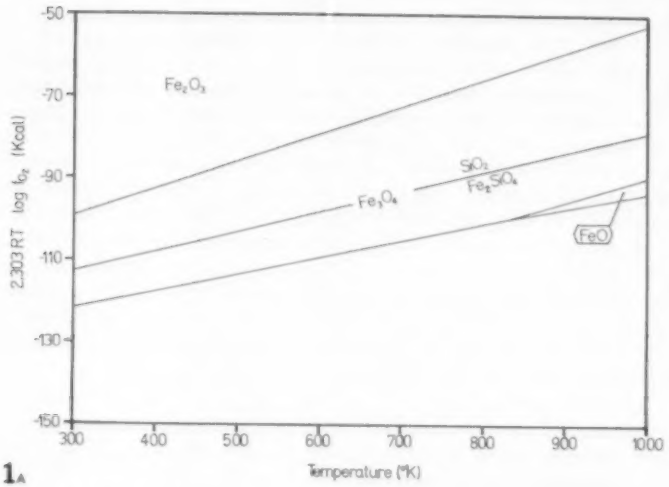


FIG. 1. Stability field of iron and of iron oxides in the Fe–O system.
FIG. 1a. Alternative plot of stability fields of iron and iron oxides in the Fe–O system.

From this it follows that the change in enthalpy for the formation of 3 mols of Fe_2O_3 is -55.0 ± 4.1 Kcal and the change in entropy -30.0 ± 2.7 cal/deg. The change in free energy is therefore:

$$\Delta G_{298} = \Delta H_{298} - T\Delta S_{298} = -55{,}000 + 30.0 \times 298 \text{ cal.} \quad (3)$$

The equilibrium constant K for the reaction is equal to $1/fo_2^{\frac{1}{2}}$ where fo_2 is the fugacity of oxygen. The free energy change is related to the equilibrium constant by the equation

$$\Delta G_T = -2.303\ RT \log K. \quad (4)$$

Thus at 298° K

$$-55{,}000 + 30.0 \times 298 = 2.303 \times R \times 298 \log fo_2^{\frac{1}{2}}. \quad (5)$$

The form of this equation is the same as that of equation 1. The values found by direct measurement at various temperatures for the terms A and B in equation 1 between 298° K and 1460° K are 59,620 cal and 33.62 cal/deg, respectively (9); for this temperature interval the oxygen fugacity between the field of stability of hematite and magnetite can be calculated from the equation

$$-59{,}620 + 33.62\ T = 2.303\ RT \log fo_2^{\frac{1}{2}}. \quad (6)$$

The uncertainty assigned to ΔG_T is ca. 8,000 cal. Since the terms in equations 5 and 6 do not differ at 298° K by more than the assigned uncertainty, the fugacity of oxygen at various temperatures at the boundary of the stability fields of two compounds could be calculated from the enthalpy and entropy data for 298° K. Unfortunately the agreement between the experimental values of the fugacity and those calculated from enthalpy and entropy data at 298° K is not always satisfactory. Thus, direct experimental data at elevated temperatures were used in the calculations in this paper wherever available, in preference to values calculated from enthalpy and entropy data at room temperature. The calculated fugacity data in those instances in which the reactions of interest have not been studied experimentally are sometimes of questionable precision. However, in the application made of the free energy data in this study uncertainties even of more than one order of magnitude in the fugacity of the gases considered do not seriously affect the conclusions.

The approach used above for the iron oxides can also be used in representing the stability field of the iron sulfides. At the boundary of the stability fields of iron and pyrrhotite, the sulfur fugacity is defined by the equilibrium constant of the reaction

$$2[Fe] + (S_2) \rightarrow 2[FeS] \quad (7)$$

and the sulfur fugacity at the boundary fields of pyrrhotite and pyrite by the equilibrium constant of the reaction

$$2[FeS] + (S_2) \rightarrow 2[FeS_2]. \quad (8)$$

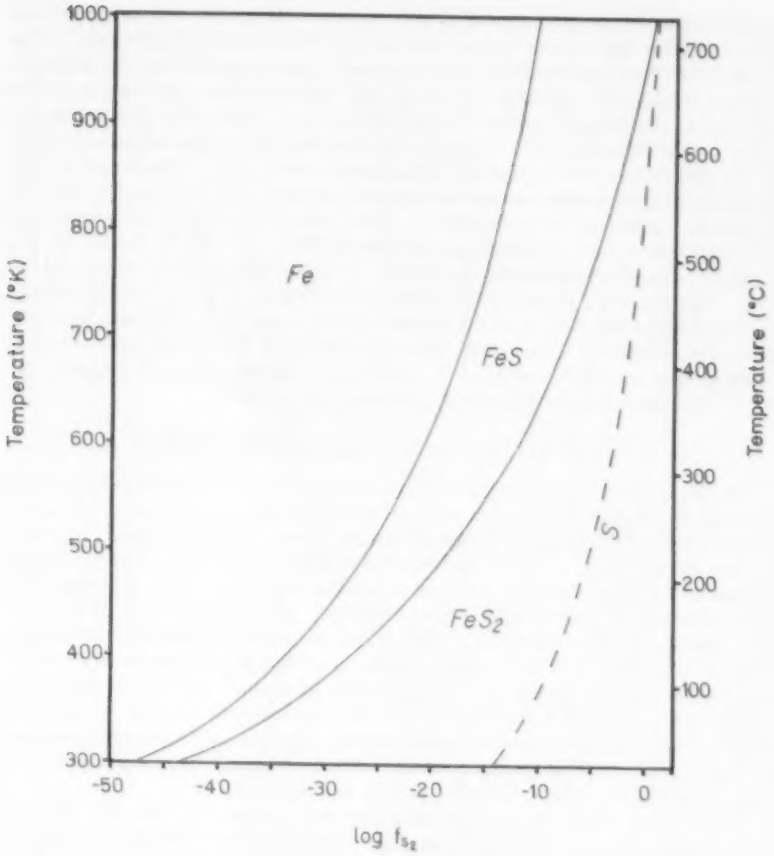


FIG. 2. Stability field of iron and iron sulfides in the Fe–S system.

Both of these reactions have been studied in some detail; the fugacity of S_2 at the boundary of the stability fields is known with good precision, and the data are shown in Figure 2. Fortunately, good data are also available for many other sulfides of importance in the study of ore deposits.

On the basis of metal-oxygen and metal-sulfur diagrams, three-dimensional diagrams can be constructed in which the axes represent the logarithm of the O_2 fugacity, the logarithm of the S_2 fugacity and the temperature, respectively. In the convention adopted here temperature has been assigned to the vertical axis. Such a diagram for iron minerals contains the stability fields of the sulfides and oxides of the metal, as well as of the native metal itself. In addition, the sulfates and any other compounds containing iron

combined with oxygen and sulfur will appear. Minerals of iron which contain volatiles other than sulfur and oxygen lie outside the diagram. The most important iron mineral thus excluded is siderite, $FeCO_3$. A different type of diagram is required to permit the representation of this mineral in relation to the sulfides, oxides and sulfates of iron. Since for such a diagram three composition axes are required (f_{CO_2}, f_{S_2}, f_{O_2}) the temperature axis of the S_2–O_2 diagrams must be replaced by a composition axis. The resulting diagrams must therefore be isothermal representations. S_2–O_2–T and S_2–O_2–CO_2 diagrams have been constructed for those metals for which sufficient data are available in such compilations as Rossini et al. (15), K. K. Kelley (7,7a), Coughlin (2a) Kubaschewski and Evans (9) and Kubaschewski and Catterall (10). Fortunately the available data are sufficient to permit the construction of diagrams for most of the important elements of metallic ore deposits. However, important gaps still exist, particularly for those minerals containing two or more metals. A complete understanding of mineral associations cannot be obtained until these gaps are filled.

THE IRON-SULFUR-OXYGEN–TEMPERATURE DIAGRAM

In the previous section the oxygen-temperature and sulfur-temperature faces of the S_2–O_2–T diagram for iron minerals were described. The completed S_2–O_2–T diagram is best built up by constructing and superimposing isothermal sections. Figure 3 shows the section at 400° K. The minimum values of log f_{O_2} and log f_{S_2} are chosen so that a portion of the stability field of native iron at this temperature is shown. Proceeding along the sulfur axis, one passes from the field of native iron to that of pyrrhotite and thence to that of pyrite. At still higher sulfur fugacities sulfur condenses. Since the temperature is above the melting point of sulfur, the condensed sulfur will be present in the liquid state. No further increase in sulfur fugacity is possible since any attempted increase merely results in a further precipitation of liquid sulfur. The appearance of condensed sulfur thus represents the upper limit of the sulfur fugacity at this temperature.

Proceeding along the oxygen axis, one passes from the stability field of iron directly into that of magnetite since wüstite is not stable at this temperature. At still higher oxygen fugacities the hematite field is reached. There is no upper boundary imposed on the oxygen fugacity as by the condensation of sulfur, since the temperature is higher than the critical temperature of oxygen. As a practical upper limit log $f_{O_2} = 0$, i.e., an oxygen fugacity of 1 atmosphere has been chosen, since oxygen compounds that are only stable at oxygen fugacities in excess of 1 atmosphere are of no interest in the study of metallic ore deposits.

Since the boundary between iron and magnetite is independent of the sulfur fugacity, this boundary is a straight line parallel to the sulfur axis in Figure 3. Similarly, since the boundary between iron and pyrrhotite is independent of the oxygen fugacity, the Fe–FeS boundary is a straight line parallel to the oxygen fugacity axis. The Fe–FeS and Fe–Fe_3O_4 boundaries together include a portion of the stability field of native iron, in particular that portion of it in which the sulfur and oxygen fugacities are largest.

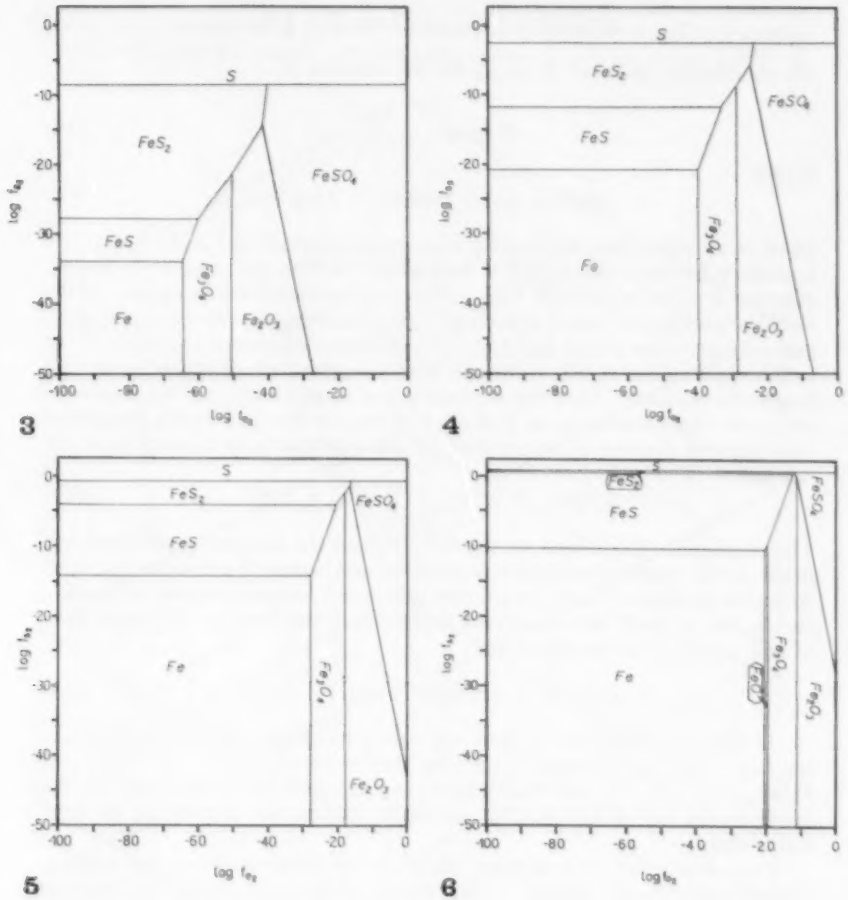


FIG. 3. Isothermal section at 400° K through the log fo_2–log fs_2–T diagram for the Fe–O–S system.

FIG. 4. Isothermal section at 600° K through the log fo_2–log fs_2–T diagram for the Fe–O–S system.

FIG. 5. Isothermal section at 800° K through the log fo_2–log fs_2–T diagram for the Fe–O–S system.

FIG. 6. Isothermal section at 1000° K through the log fo_2–log fs_2–T diagram for the Fe–O–S system.

The boundary between pyrrhotite and magnetite is a straight line whose slope is determined by the form of the equilibrium constant for the equation

$$3[FeS] + 2(O_2) \rightarrow [Fe_3O_4] + \tfrac{3}{2}(S_2) \tag{9}$$

the equilibrium constant K_{PH-MT} for the reaction is

$$K_{PH-MT} = \frac{f_{(S_2)}^{\frac{3}{2}}}{f_{(O_2)}^{2}} \tag{10}$$

so that

$$\log K_{PH-MT} = \tfrac{3}{2} \log f_{S_2} - 2 \log f_{O_2}. \tag{11}$$

Since in an isothermal section, $\log K_{PH-MT}$ is constant in Figure 3, and the boundary between the stability field of pyrrhotite and magnetite in this diagram is a line with slope 1.33. This line intersects the boundary of the FeS–FeS_2 fields and terminates there. At its termination pyrite, pyrrhotite, and magnetite are stable together. The boundary between the fields of the sulfides and oxides of iron continues with a segment along which pyrite and magnetite coexist. That the boundary is a straight line can be shown by using the same reasoning as that used above for the FeS–Fe_3O_4 boundary. The slope of the line is determined by the coefficients of O_2 and S_2 in the reaction

$$3[FeS_2] + 2(O_2) \rightarrow [Fe_3O_4] + 3(S_2). \tag{12}$$

The coexistence line intersects the boundary of the magnetite and hematite fields; at the intersection pyrite, magnetite, and hematite are stable together. At higher oxygen and sulfur fugacities pyrite and hematite can exist together stably, the slope of the coexistence line being determined by the coefficients of (S_2) and (O_2) in the equation

$$2[FeS_2] + \tfrac{3}{2}(O_2) \rightarrow [Fe_2O_3] + 2(S_2). \tag{13}$$

At appreciably higher oxygen and sulfur fugacities the field of $FeSO_4$ is reached. This is bounded in part by the coexistence curve of Fe_2O_3 and $FeSO_4$, in part by the coexistence curve of FeS_2 and $FeSO_4$ and in part by the condensation line of liquid sulfur, which terminates the diagram at the high sulfur side.

Data for other iron compounds such as ferric sulfate, the sulfites, thiosulfates, etc. are lacking. They do not occur in hypogene ore deposits and are of no interest in this study.

We find, therefore, that the portion of the sulfur-oxygen diagram under consideration is divided into a number of fields in which a given iron mineral is stable, certain lines along which various pairs of minerals are stable, and a number of points at which three minerals coexist at equilibrium. It is reassuring that the commonly observed pairs FeS–Fe_3O_4, FeS_2–Fe_3O_4, FeS_2–Fe_2O_3 are predicted by the diagram. The sulfate field is of no particular interest since anhydrous $FeSO_4$ does not occur as a mineral, but it suggests, and indeed occupies at low temperatures, the area of naturally occurring secondary iron minerals.

Isothermal sections at 600°, 800° and 1,000° K have been similarly constructed and are shown in Figures 4, 5 and 6. The major changes that take place as the temperature is increased are an increase in the size of the native iron field, a corresponding shift of the phase boundaries of oxides and sufides to higher f_{O_2} and f_{S_2} values, and the appearance of wüstite in the 1,000° K section.

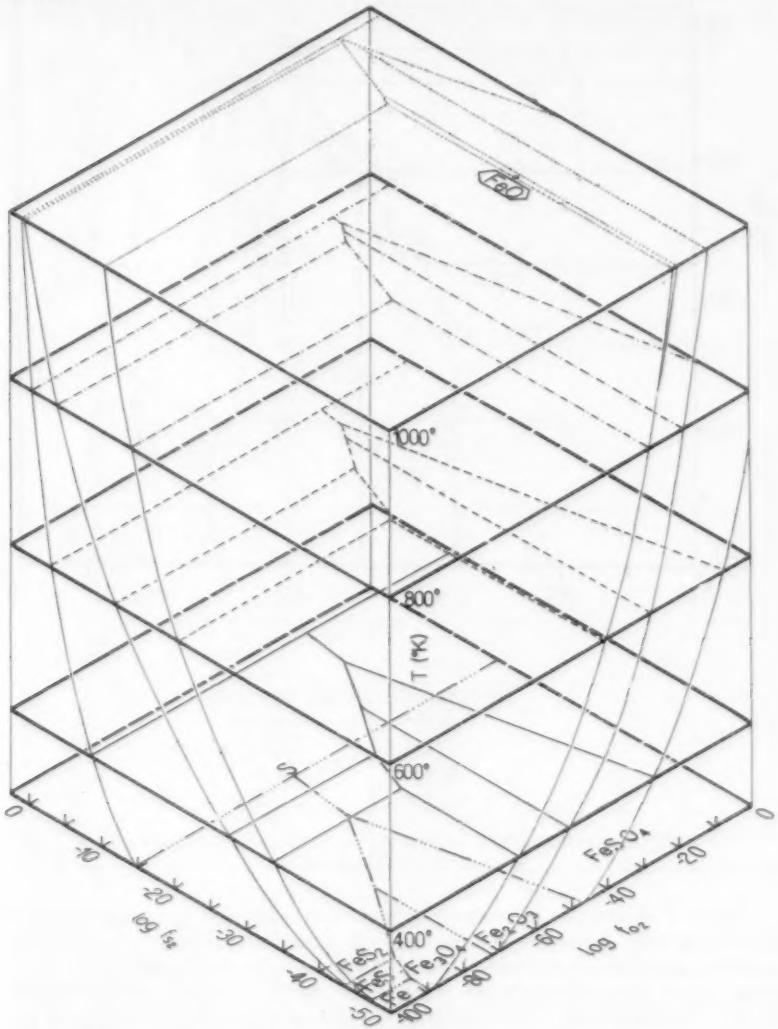


FIG. 7. The log f_{O_2}–log f_{S_2}–T diagram for the Fe–O–S system.

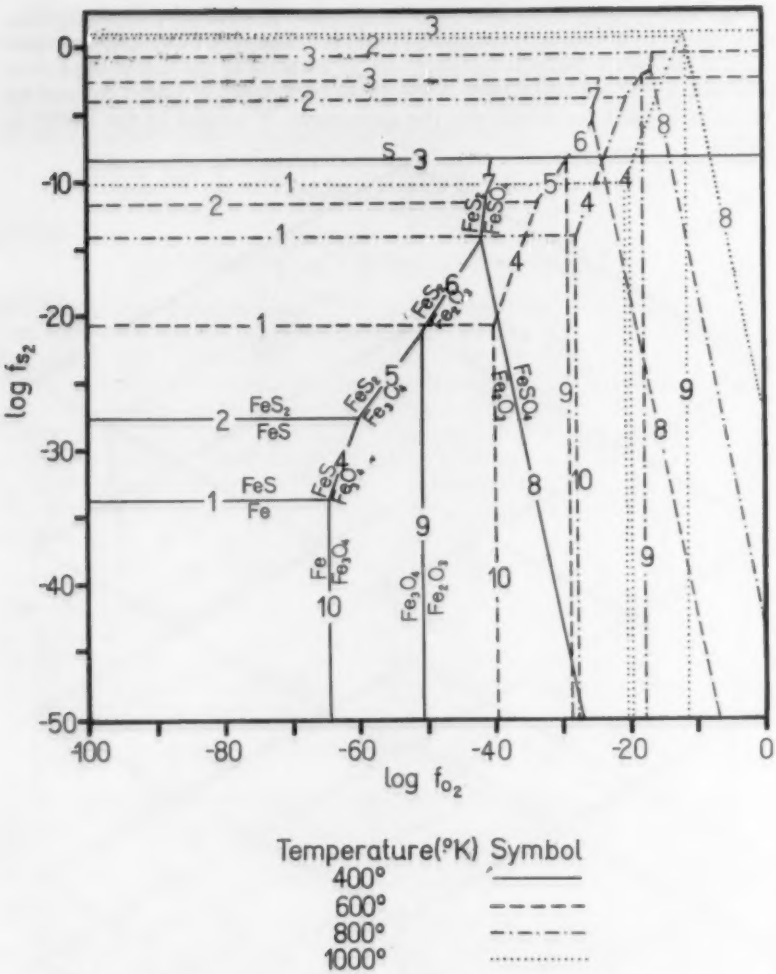


FIG. 8. Projection of the log fo_2–log fs_2–T diagram for the Fe–O–S system on the basal plane.

Figure 7 shows the isothermal sections superimposed in a three-dimensional diagram. Space is divided into the stability volumes of individual minerals, surfaces along which two minerals coexist in equilibrium, lines along which three minerals are stable and a point at which four minerals coexist at equilibrium. The stability volume of native iron is bounded by two surfaces each parallel to one of the composition axes and meeting in a curve which sweeps towards lower values of the sulfur and oxygen fugacities

with falling temperature. The boundaries between sulfides and oxides of iron consist of a series of non-vertical surfaces.

A more convenient representation of the completed diagram is shown in Figure 8 in which the isothermal sections of Figures 3, 4, 5 and 6 are plotted in a single diagram. This figure is thus a projection of the S_2–O_2–T diagram of Figure 7 on the S_2–O_2 plane. It is believed that the changes in the stability fields of the various compounds with changing temperature can be

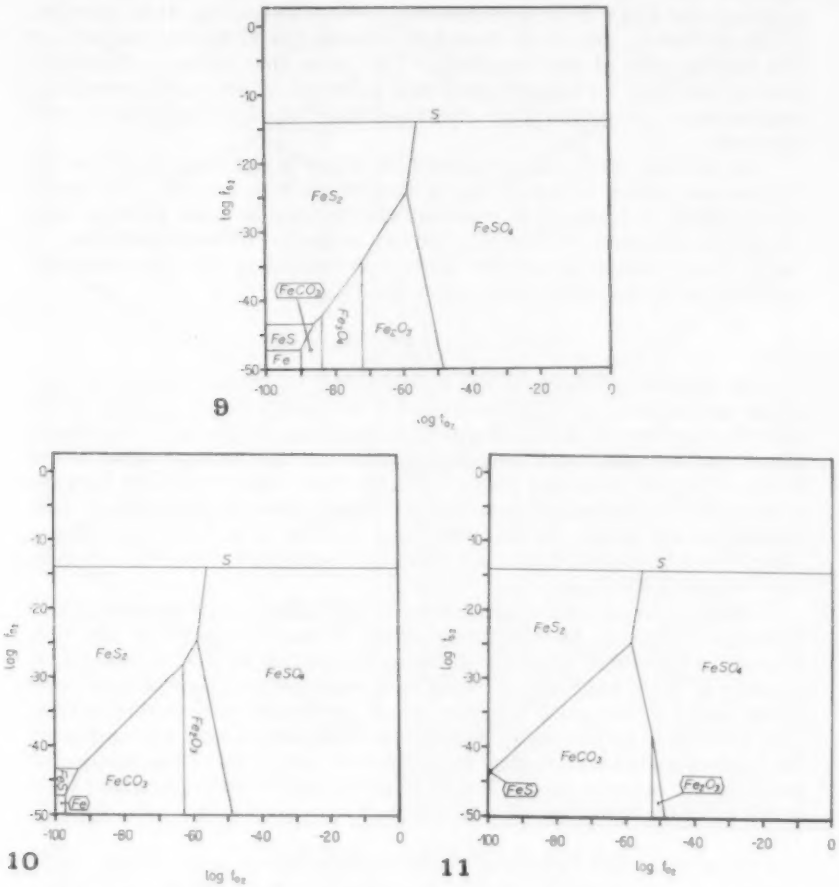


FIG. 9. Isobaric section ($f_{CO_2} = 10^{-3.5}$ atm) through the log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Fe–O–S–C system at 300° K.

FIG. 10. Isobaric section ($f_{CO_2} = 1.0$ atm) through the log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Fe–O–S–C system at 300° K.

FIG. 11. Isobaric section ($f_{CO_2} = 1000$ atm) through the log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Fe–O–S–C system at 300° K.

seen more easily in this figure, and this type of representation has been adopted for the other metal–sulfur–oxygen systems.

Data for only one geologically important reaction involving an iron oxide and an iron silicate are available, i.e., the reaction between fayalite and oxygen to form magnetite and quartz. Since magnetite is stable in the presence of fayalite as well as in the presence of quartz, the boundary between the stability fields of fayalite and quartz must lie within the magnetite stability field. Its position is indicated in Figures 1 and 1a and can be seen to bisect the Fe_3O_4 field approximately. Fayalite-bearing rocks therefore lie on the low-f_{O_2} side of the boundary whereas quartz bearing rocks lie on the high-f_{O_2} side of the boundary. The curve thus forms a convenient low-f_{O_2} boundary for hydrothermal vein solutions, in which the assemblage quartz-magnetite rather than the assemblage fayalite-magnetite is predominant.

The position of the olivine-quartz boundary is not independent of the magnesium content of the olivine in equilibrium with quartz. The theory of this effect is discussed in standard thermodynamic texts and has been applied by Sahama and Torgeson (16) to a somewhat different problem. It can be shown that no appreciable shifts in the boundary take place until the composition of the olivine approaches $Fo_{50}Fa_{50}$.

THE Fe–S_2–O_2–CO_2 DIAGRAMS

The relationship between the stability field of siderite to that of iron oxides and sulfides can be demonstrated in isothermal diagrams along whose axes the logarithm of the S_2, O_2 and CO_2 fugacities are plotted. The ranges chosen for the sulfur and oxygen fugacities are the same as those in the S_2–O_2–T diagram described above. For the lower limit of the CO_2 fugacity a value of $10^{-3.5}$ has been chosen; this is somewhat less than atmospheric CO_2 pressure at sea level. As the upper limit a value of 10^{+3} has been chosen since it is to be expected that the CO_2 fugacity in ore forming fluids hardly ever exceeds 1,000 bars.

The three-dimensional diagrams can be built up in a manner analogous to that just discussed, by the superposition of sections in which the CO_2 fugacity is constant. Figure 9 shows such a section at 300° K and a CO_2 fugacity of $10^{-3.5}$ atmosphere. It is to be expected that assemblages commonly found at the earth's surface would be encountered in this section. This is found to be the case. The siderite field is small, and encroaches on the fields of native iron, magnetite, pyrrhotite, and pyrite. The position of the boundary between siderite and its neighbors is determined by equilibrium in the following reactions:

$$[Fe] + (CO_2) + \tfrac{1}{2}(O_2) \rightarrow [FeCO_3] \tag{14}$$

$$[Fe_3O_4] + 3(CO_2) \rightarrow 3[FeCO_3] + \tfrac{1}{2}(O_2) \tag{15}$$

$$[FeS] + (CO_2) + \tfrac{1}{2}(O_2) \rightarrow [FeCO_3] + \tfrac{1}{2}(S_2) \tag{16}$$

$$[FeS_2] + (CO_2) + \tfrac{1}{2}(O_2) \rightarrow [FeCO_3] + (S_2). \tag{17}$$

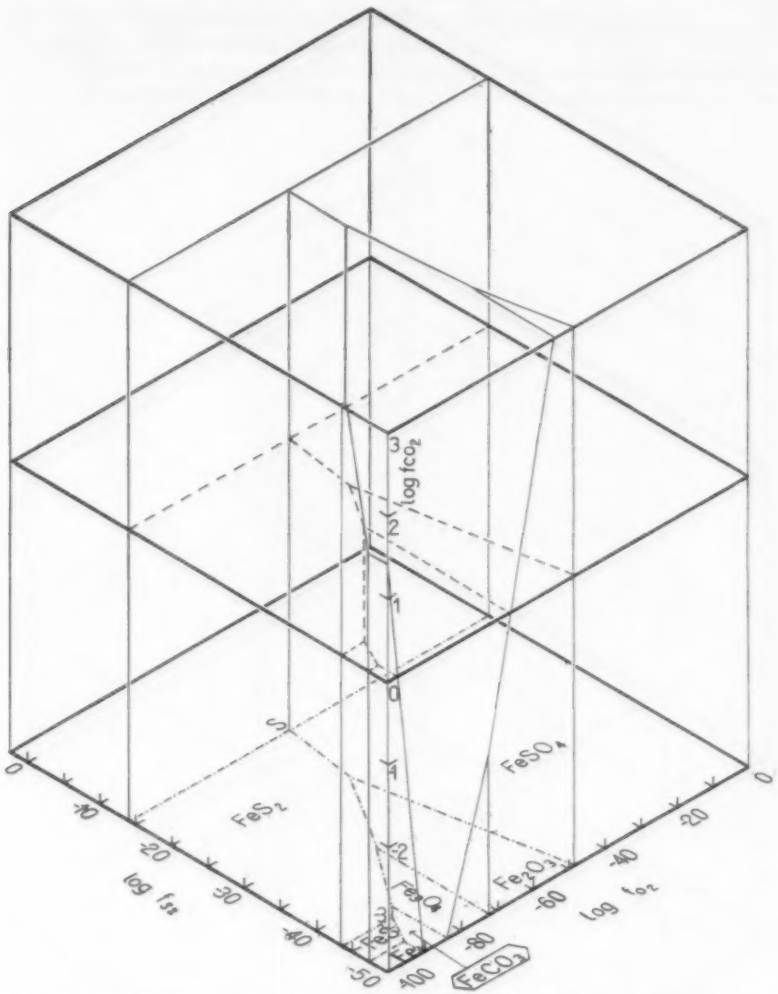


FIG. 12. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Fe–O–S–C system at 300° K.

There are no common boundaries between siderite and hematite or between siderite and $FeSO_4$ at this temperature and CO_2 fugacity.

Figures 10 and 11 are sections similar to those in Figure 9, but calculated for CO_2 fugacities of 1 and 1,000 atmospheres, respectively. The siderite field is seen to increase in size with an increase in CO_2 fugacity. In Figure 10 the magnetite field has completely disappeared, and a common boundary

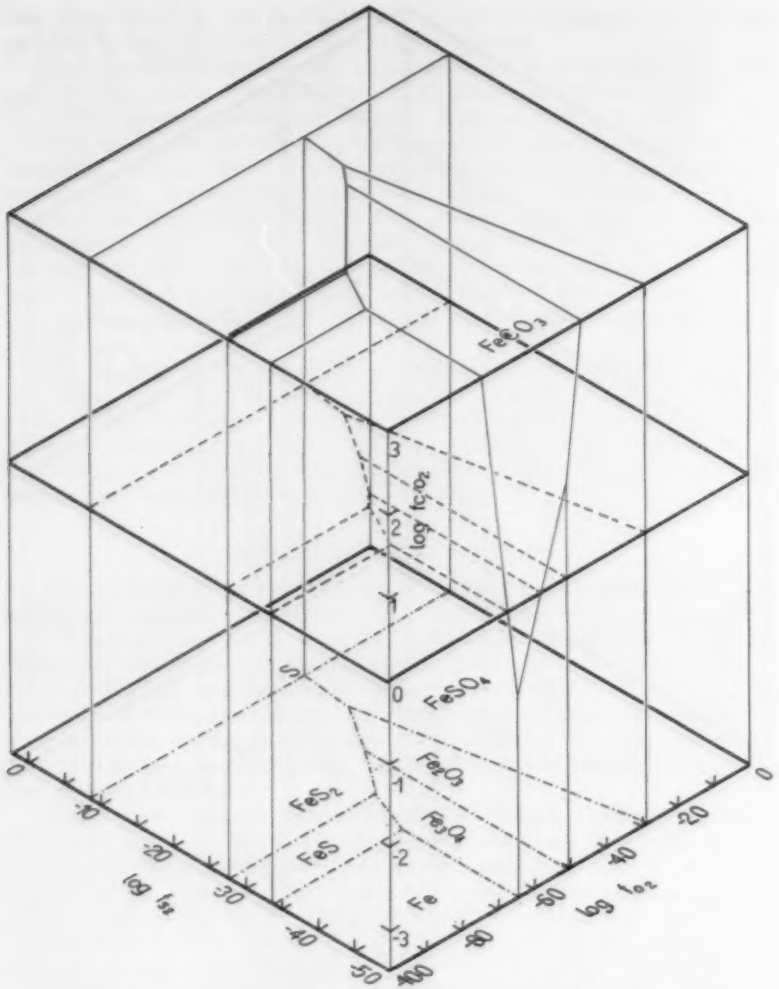


FIG. 13. The log fo_2–log fs_2–log fco_2 diagram for the Fe–O–S–C system at 400° K.

exists at this value of the CO_2 fugacity between siderite and hematite. In Figure 11 much of the hematite field has been similarly usurped by that of siderite and there is a common boundary between siderite and $FeSO_4$ at this value of the CO_2 fugacity. As the CO_2 fugacity increases, the stability fields of Fe, FeS, and FeS_2 are reduced in size, so that at a CO_2 fugacity of 10^{+3} atmospheres, the Fe field no longer includes those values of the oxygen

and sulfur fugacities shown in the diagram, and only a small corner of the FeS stability field remains in the diagram.

In Figure 12 the three previous diagrams have been superimposed to form the completed S_2–O_2–CO_2 diagram at 300° K. The tapering of the

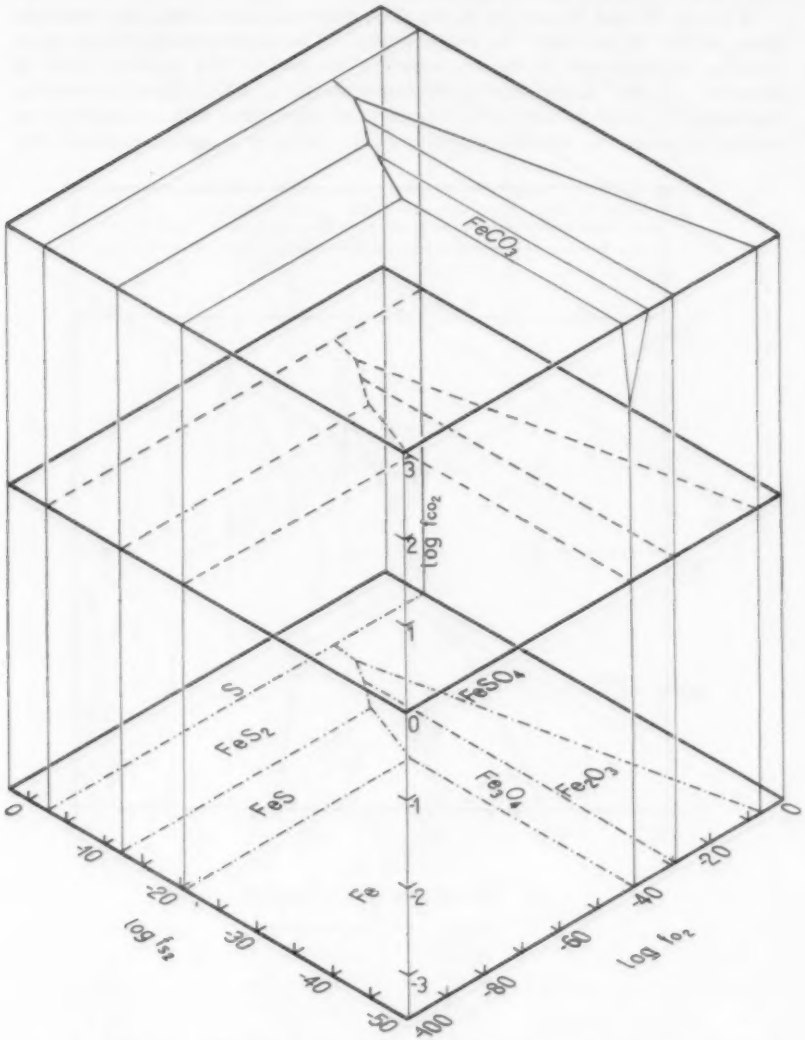


FIG. 14. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Fe–O–S–C system at 600° K.

siderite stability field toward lower values of the CO_2 fugacity is evident. At CO_2 fugacities lower than those shown in Figure 12 the siderite stability field reduces to a horizontal line and ultimately disappears completely. This behavior is somewhat different from that of such carbonates as $ZnCO_3$, $PbCO_3$, and $MnCO_3$ as discussed below.

Figures 13 and 14 are Fe–S_2–O_2–CO_2 diagrams calculated for temperatures of 400° K and 600° K, respectively. The most striking effect of increasing temperature is the decrease in the size of the stability field of siderite. At 400° K the siderite field pinches out at a CO_2 fugacity near 0.1 atmosphere, while at 600° K a fugacity of more than 100 atmospheres is needed to enter the siderite stability field. This is in agreement with the

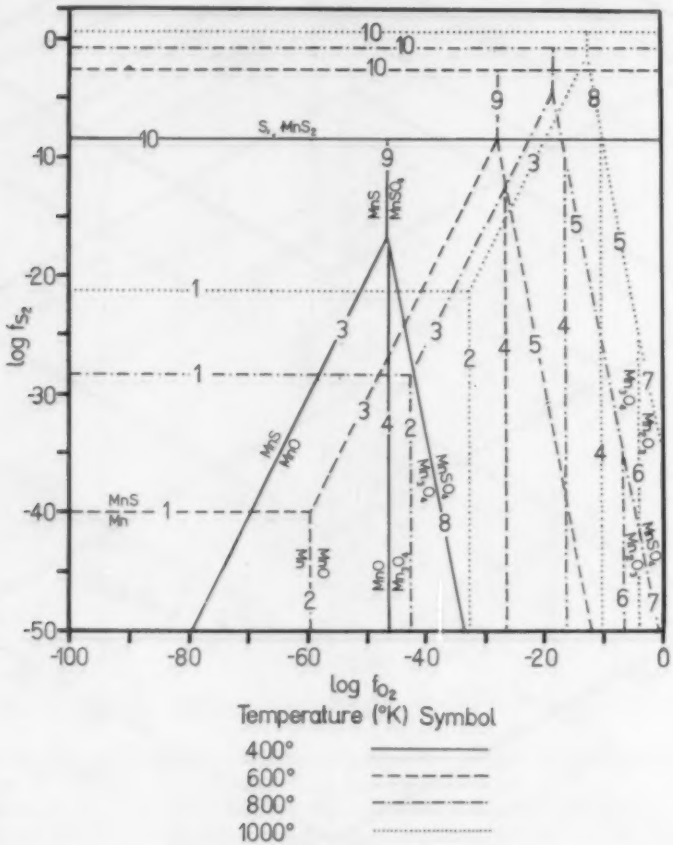


FIG. 15. Projection of the log fo_2–log fs_2–T diagram for the Mn–O–S system on the basal plane.

field observation that siderite is best represented in medium- and low-temperature ore deposits and tends to occur only late in the sequence of deposition of high-temperature deposits. It is also of interest to note that the assemblages pyrrhotite–siderite and pyrite–siderite are permitted at 400° K at reasonably low CO_2 fugacities, in agreement with field observation on siderite veins.

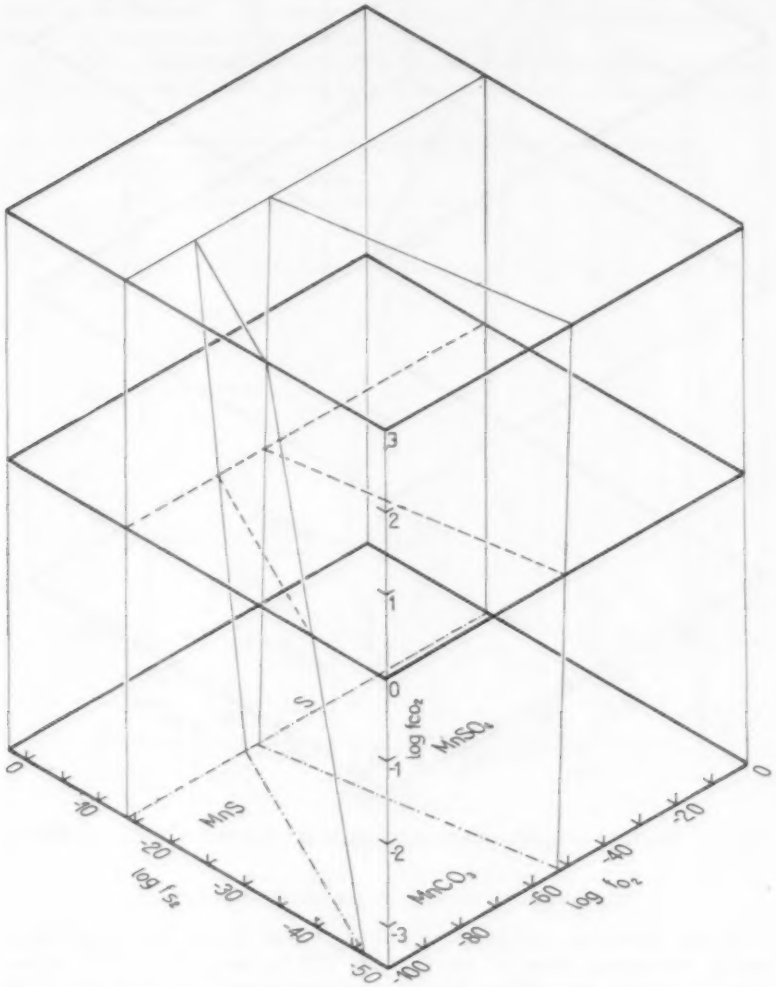


FIG. 16. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Mn–O–S–C system at 300° K.

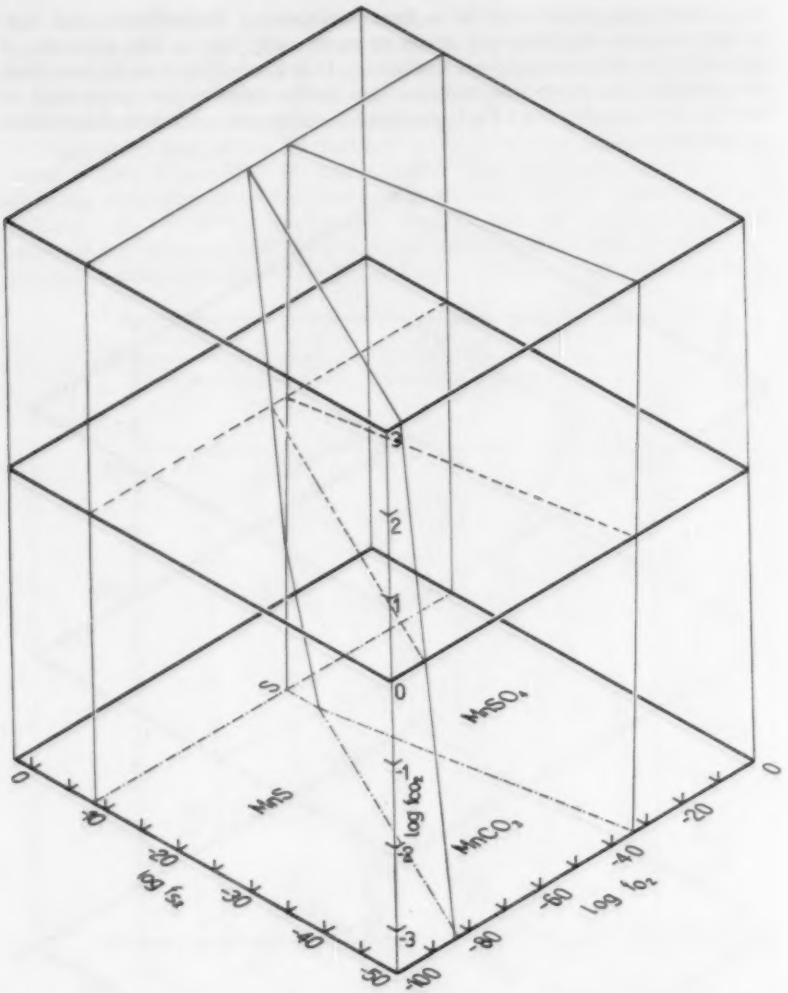


FIG. 17. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Mn–O–S–C system at 400° K.

THE STABILITY FIELDS OF MANGANESE MINERALS

In the following discussion the S_2–O_2–T and S_2–O_2–CO_2 diagrams of metals commonly found in ore deposits will be presented. The accompanying descriptions will be brief since the construction and most of the features of the diagrams have counterparts in those of the corresponding

diagrams for the iron minerals. An analysis of the diagrams in terms of the field occurrences of the minerals is reserved for the second of this pair of papers.

Figure 15 is a projection on the S_2–O_2 plane of the S_2–O_2–T diagram for manganese minerals, and is thus analogous to Figure 8 for iron minerals. The field of native manganese is present at all but the lowest temperature. Alabandite, MnS, manganosite, MnO, and hausmannite, Mn_3O_4, cover much of the diagram. No common boundaries between alabandite and the higher oxides exist since the field of $MnSO_4$ intervenes.

At 400° K the field of bixbyite, $(Fe, Mn)_2O_3$ and of the dioxides polianite, pyrolusite and ramsdellite do not appear on the diagram. Their appearance

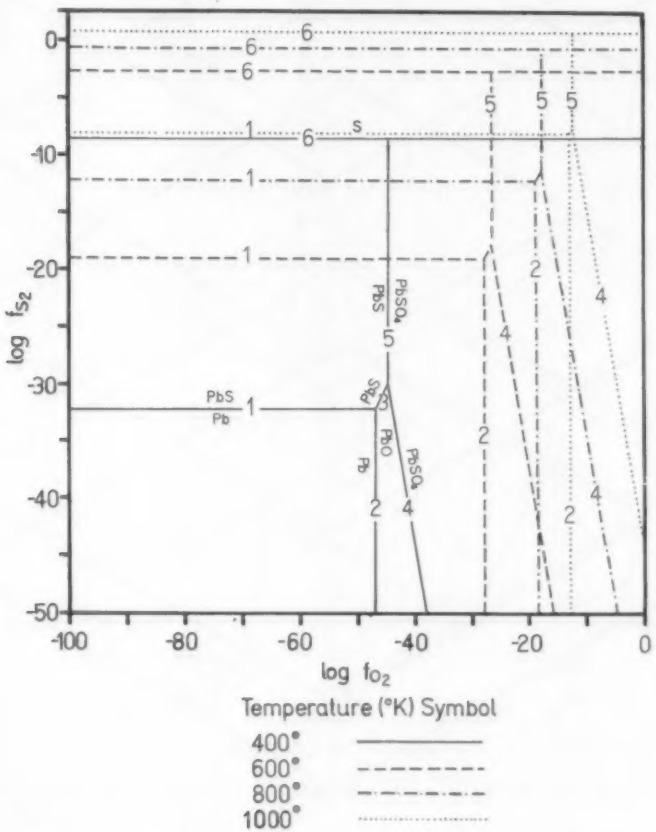


FIG. 18. Projection of the log fo_2–log fs_2–T diagram for the Pb–O–S system on the basal plane.

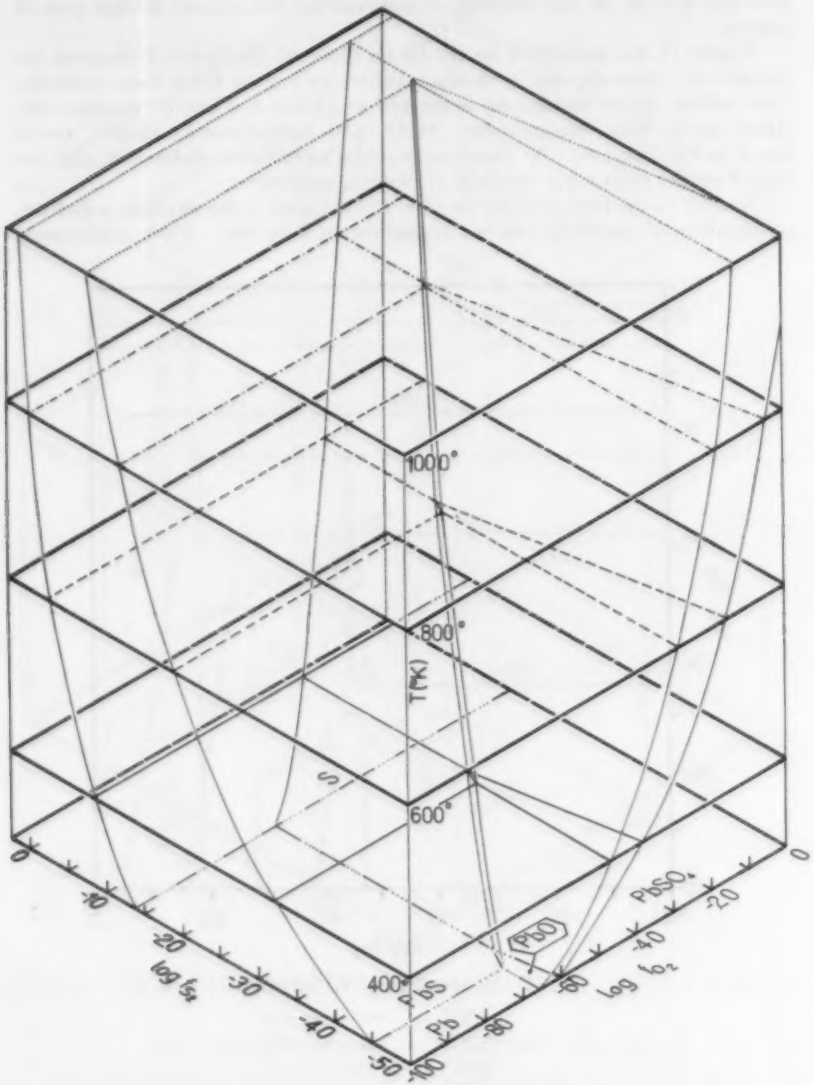


FIG. 19. The log fo_2–log fs_2–T diagram for the Pb–O–S system.

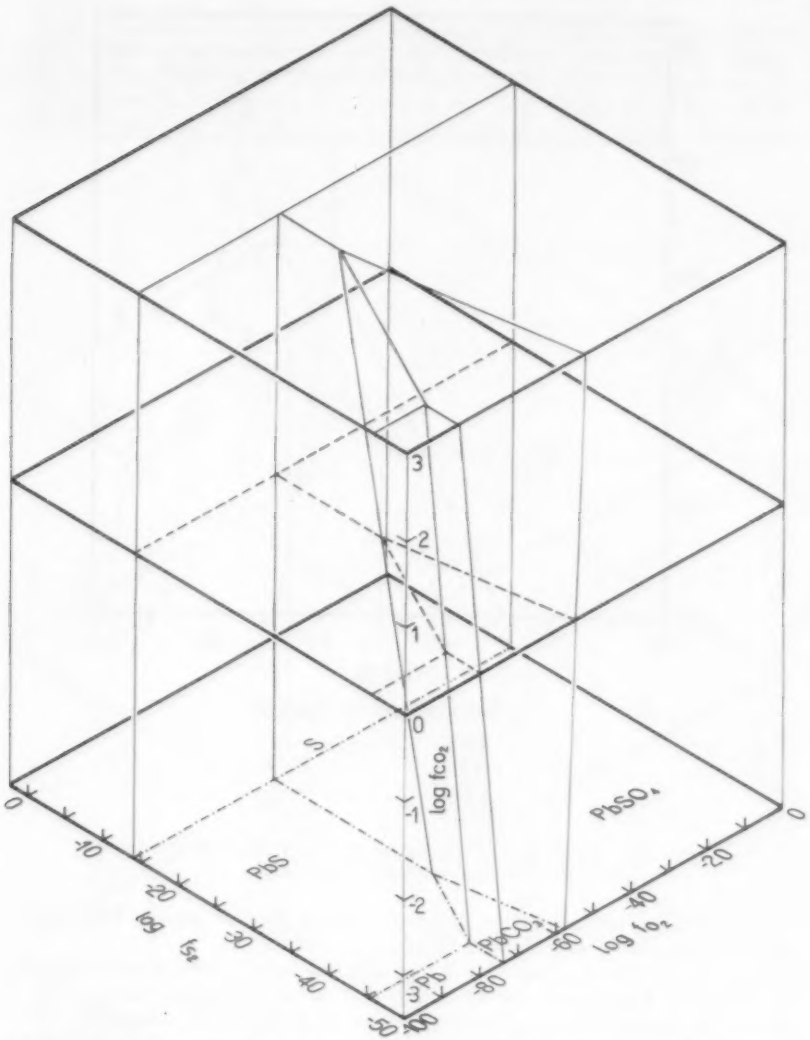


FIG. 20. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Pb–O–S–C system at 300° K.

demands lower sulfur fugacities than those represented on the diagram, except at higher temperatures.

The disulfide, hauerite, MnS_2, is apparently only just stable in this temperature range (2) with respect to MnS and sulfur and is to be expected only very close to the condensation plane of sulfur. The dimensions of its

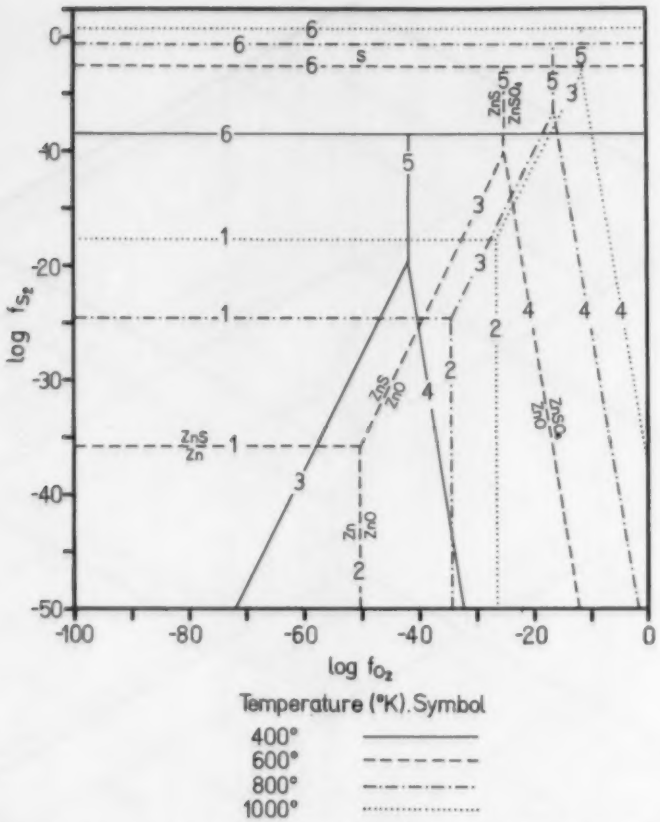


FIG. 21. Projection of the log fo_2–log fs_2–T diagram for the Zn–O–S system on the basal plane.

field of stability are not known precisely and its appearance has been indicated as coinciding with the condensation of sulfur.

The S_2–O_2–CO_2 diagrams for manganese minerals at 300° K and 400° K are shown in Figures 16 and 17. The field of manganosite, MnO is completely preempted by that of rhodochrosite, $MnCO_3$. With increasing CO_2 fugacity the rhodochrosite field is enlarged at the expense of the stability fields of alabandite and $MnSO_4$. With increasing temperature and at a given CO_2 fugacity the rhodochrosite field is decreased and shifted to higher O_2 and lower S_2 fugacities.

THE STABILITY FIELDS OF LEAD MINERALS

In the S_2–O_2–T projection and in the S_2–O_2–T diagram for lead minerals of Figures 18 and 19 the stability field of native lead is present at all temper-

atures. Galena, PbS, the only sulfide, has a large stability field bounded at high oxygen fugacities by the field of massicot, PbO, and anglesite, $PbSO_4$. The stability fields of the higher oxides, minimum, Pb_3O_4, the oxide Pb_2O_3, and plattnerite, PbO_2, do not fall within the limits of the S_2–O_2 diagram of Figure 18 and they are thus in the same category as the higher manganese

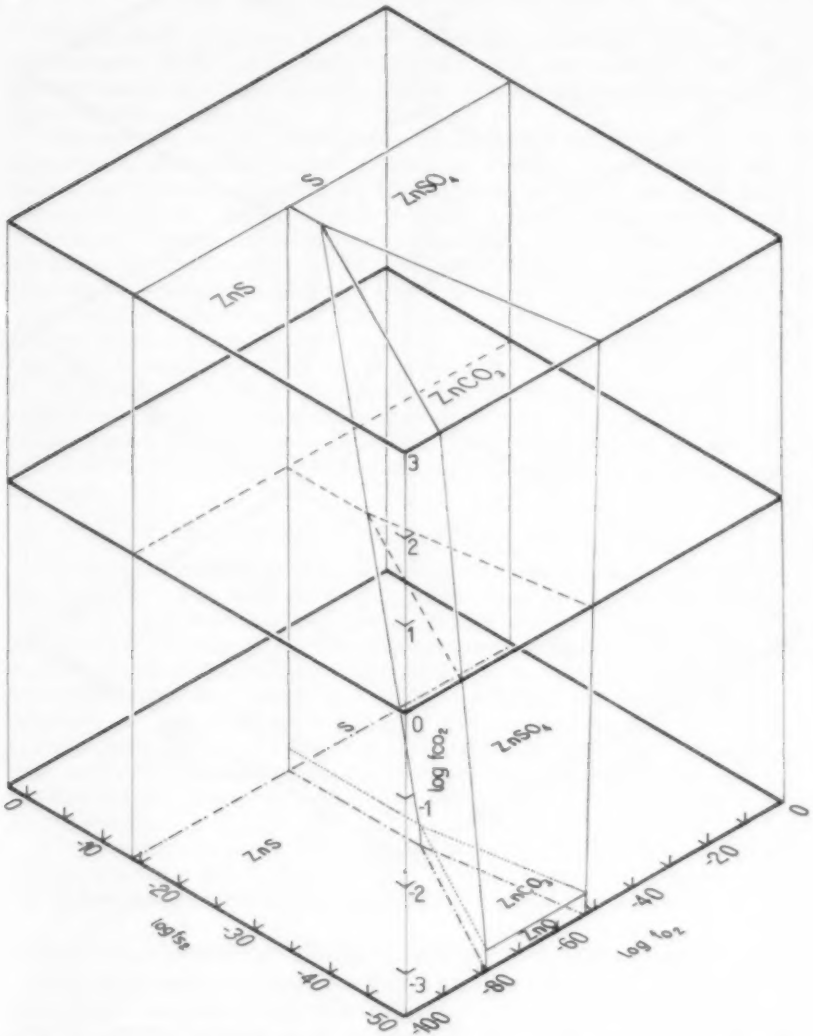


FIG. 22. The log fo_2–log fs_2–log fco_2 diagram for the Zn–O–S–C system at 300° K.

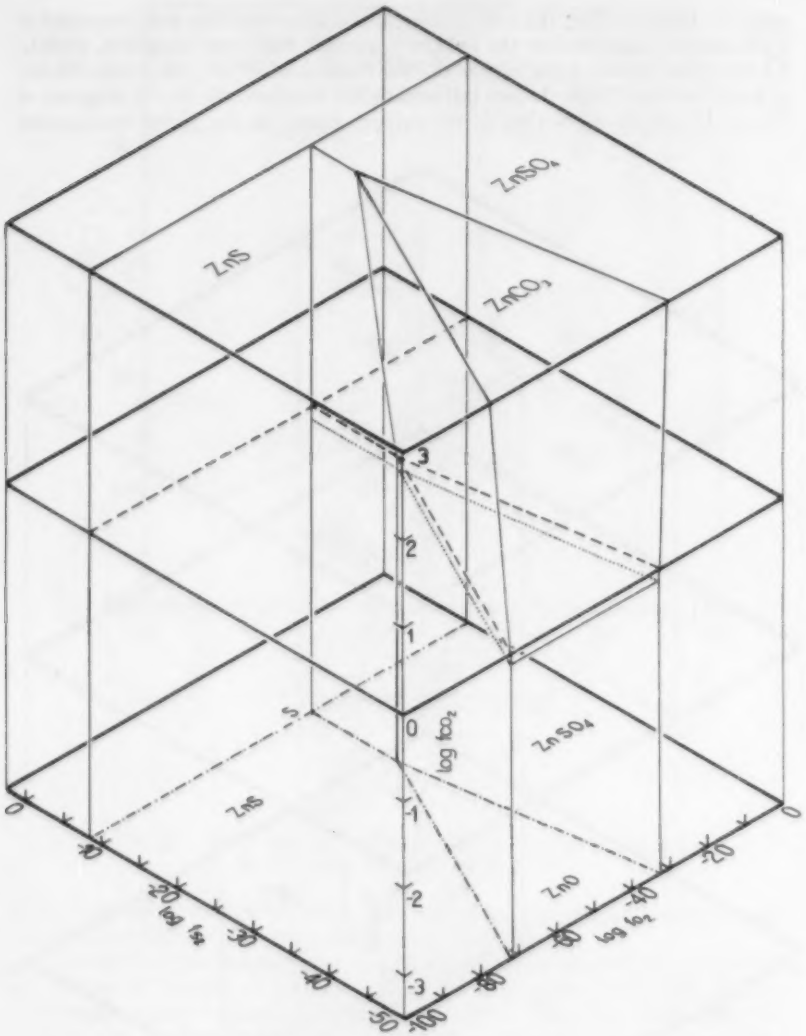


FIG. 23. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Zn–O–S–C system at 400° K.

oxides discussed above. The mineral lanarkite, $PbO.PbSO_4$, is not shown in the diagram since the necessary thermodynamic data are not available. Its stability field must straddle the PbO–$PbSO_4$ boundary in Figures 18 and 19. The strip in which the mineral is stable is probably narrow. Other oxy-sulfates of lead exist but have not been discovered as minerals.

The relationship of cerussite, $PbCO_3$, to the lead minerals shown in Figure 18 is shown in Figure 20 for 300° K. Even at the lowest CO_2 fugacity in the diagram cerussite is stable. It occupies the field of PbO and encroaches on the fields of Pb, PbS and $PbSO_4$ to an extent which increases with CO_2 fugacity.

THE STABILITY FIELD OF ZINC MINERALS

The S_2–O_2–T projection for zinc includes sphalerite, ZnS, zincite, ZnO, and zinkosite, $ZnSO_4$, as shown in Figure 21. It is very similar to that for the corresponding manganese minerals, but is not complicated by the presence of higher oxides.

However the S_2–O_2–CO_2 diagrams are somewhat different for the two metals since the stability field of smithsonite, $ZnCO_3$, is much smaller than that of rhodochrosite, as shown by the diagrams for 300° K and 400° K of Figures 22 and 23. At 300° K ZnO is stable at CO_2 fugacities smaller than $10^{-9.2}$ atm. Thus at the base plane of Figure 22, ZnS, ZnO, and $ZnSO_4$ are the stable zinc compounds. If the fugacity of CO_2 is raised, the zincite field becomes the smithsonite field at a CO_2 fugacity of $10^{-9.2}$ atmosphere. At CO_2 fugacities higher than $10^{-9.2}$ the stability field of smithsonite flares out at the expense of the fields of sphalerite and zinkosite. At 400° K the lower limit of CO_2 fugacity at which $ZnCO_3$ is stable is $10^{-0.1}$ atm. The raising of the ZnO stability "ceiling" is equivalent to the progressively higher CO_2 fugacities at which the pinchout of the siderite field occurs with increasing temperature. That siderite "pinches out" whereas smithsonite "floors out" is due to the instability of FeO and the stability of ZnO at the given temperatures.

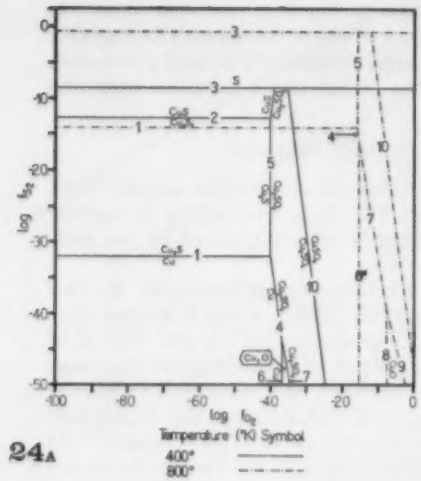
THE STABILITY FIELD OF COPPER MINERALS

Data on the sulfides, oxides, and sulfates of copper are shown in Figures 24a and 24b. The diagram is incomplete since the system chalcocite-digenite has not been explored from a thermochemical point of view with any degree of precision (10). The field now assigned to chalcocite is actually the field of chalcocite, Cu_2S, and digenite, Cu_9S_5, combined. The boundary between the sulfides, oxides, and sulfates of copper are thus not known precisely. It seems probable, however, that the digenite field will cover approximately half of the field now assigned to chalcocite (10). Entropy data for Cu_2SO_4 are not available; the entropy value of Ag_2SO_4 was used in the calculations, and the extent of the sulfate fields are thus known only approximately.

The monoxide, tenorite, CuO, does not occur at 400° K in the portion of the sulfur–oxygen field shown in Figure 24a. It is similar in this regard to the higher oxides of manganese and lead.

THE STABILITY FIELDS OF NICKEL MINERALS

Figure 25 shows the stability fields of nickel minerals in the S_2–O_2–T projection. The lowest sulfide is heazlewoodite, Ni_3S_2. Ni_6S_5 is not known as a mineral. The lower limit of the stability field of millerite, NiS, is shown, but data are not available for its upper limit, given by the boundary



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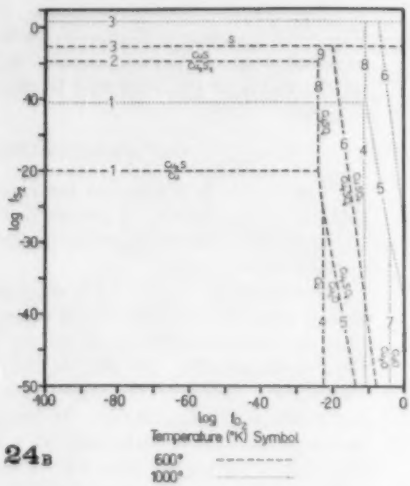

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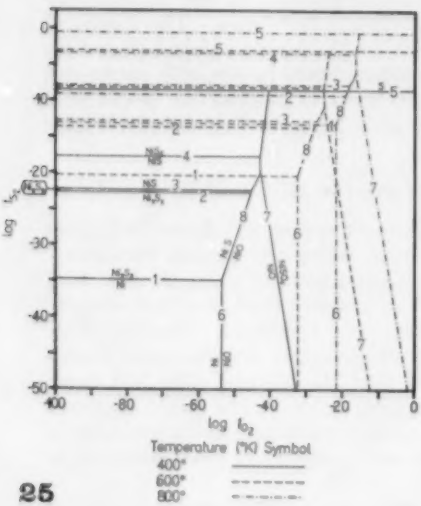

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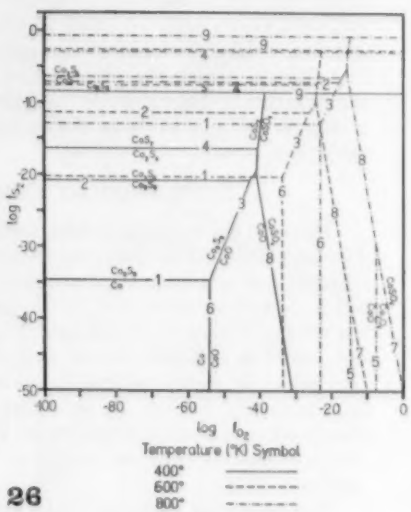

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FIG. 24a. Projection of log fo_2–log fs_2–T diagram for the Cu–O–S system on the basal plane.

FIG. 24b. Projection of the log fo_2–log fs_2–T diagram for the Cu–O–S system on the basal plane.

FIG. 25. Projection of the log fo_2–log fs_2–T diagram for the Ni–O–S system on the basal plane.

FIG. 26. Projection of the log fo_2–log fs_2–T diagram for the Co–O–S system on the basal plane.

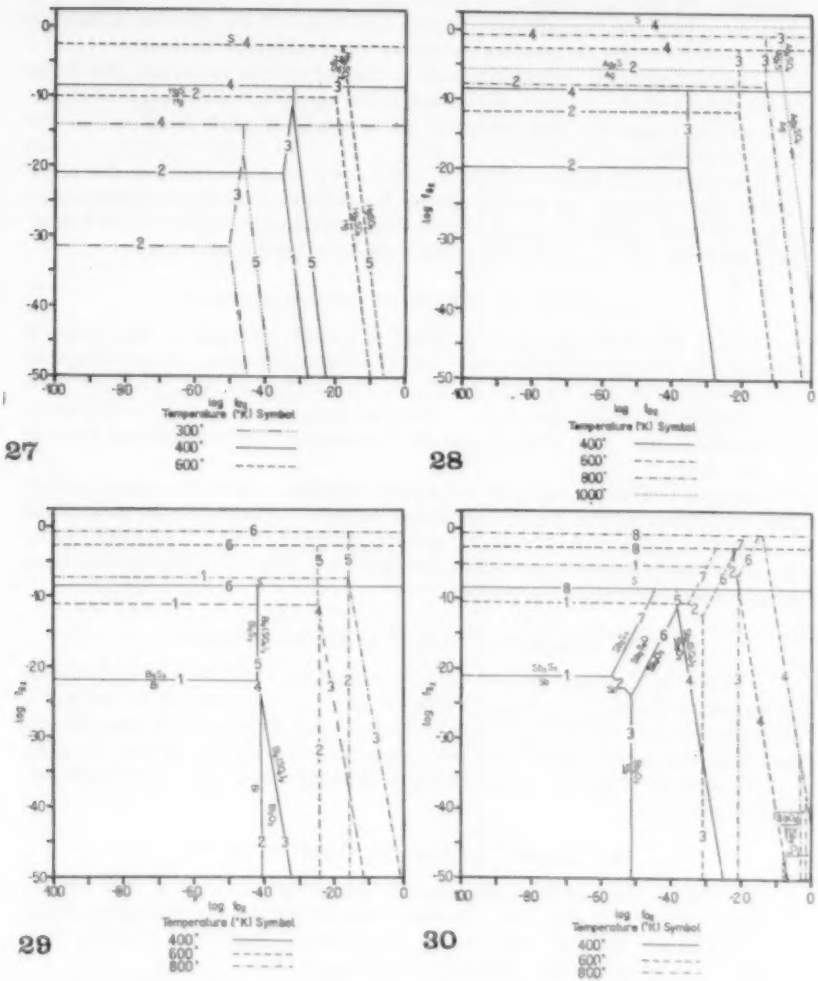


FIG. 27. Projection of the log fo_2–log fs_2–T diagram for the Hg–O–S system on the basal plane.

FIG. 28. Projection of the log fo_2–log fs_2–T diagram for the Ag–O–S system on the basal plane.

FIG. 29. Projection of the log fo_2–log fs_2–T diagram for the Bi–O–S system on the basal plane.

FIG. 30. Projection of the log fo_2–log fs_2–T diagram for the Sb–O–S system on the basal plane.

between the stability field of millerite and that of polydymite, Ni_3S_4. The boundary between the polydymite field and that of NiS_2, vaesite, is also not known, so that the diagram as shown leaves much to be desired.

The rare mineral bunsenite, NiO, is the only oxide of nickel; the limits of its stability field in Figure 25 are somewhat uncertain since, particularly at low temperatures, the free energy of formation of the sulfides is not known with precision.

The anhydrous sulfate $NiSO_4$, is not known as a mineral but the hexa- and hepta-hydrates are known as the minerals retgersite and morenosite, respectively. Similarly, the only anhydrous carbonate of nickel is not known as a mineral, and no S_2–O_2–CO_2 diagrams have been constructed.

THE STABILITY FIELDS OF COBALT MINERALS

Figure 26 shows the stability fields of Cobalt minerals in the S_2–O_2–T projection. Co_9S_8 and CoS_{1+x} are not known as minerals; the questionable mineral jaipurite may be CoS (6a) Co_3S_4, linnaeite and CoS_2, cattierite have been found as natural products. The field boundaries in the Co–S system are better known than those in the Ni–S system at temperatures of interest in this study.

Neither CoO nor Co_3O_4 are known as minerals. As in the case of nickel, the anhydrous sulfate is not known as a mineral. However, the anhydrous carbonate $CoCO_3$ is known as the mineral cobaltocalcite. Thermodynamic data for this compound are incomplete and no S_2–O_2–CO_2 diagram has been constructed for cobalt compounds.

THE STABILITY FIELD OF MERCURY MINERALS

The S_2–O_2–T projection for mercury, cinnabar, HgS, Hg_2SO_4 and $HgSO_4$ is shown in Figure 27. It is of interest that in this portion of the S_2–O_2 field the stability field of Hg_2O and of montroydite, HgO, are not represented, but that the native metal can be in equilibrium with the sulfate Hg_2SO_4.

No data on mercury carbonates are available, and none have been observed as minerals.

THE STABILITY FIELD OF SILVER MINERALS

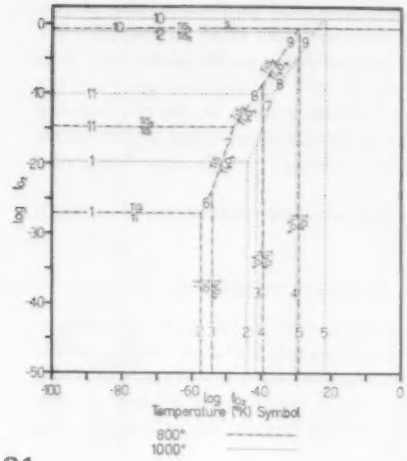
The S_2–O_2–T projection of Figure 28 for silver minerals is very similar to the projection for mercury. Native silver, argentite and acanthite, Ag_2S, and Ag_2SO_4 are the only compounds represented. Again the stability field of the oxide is completely absent in the diagram.

Data are available for Ag_2CO_3 but caluclations show that this compound is thermodynamically unstable at 300° K and at higher temperatures, even at high CO_2 fugacities.

THE STABILITY FIELD OF BISMUTH MINERALS

The S_2–O_2–T projection for bismuth minerals is shown in Figure 29. Bismuthinite, Bi_2S_3, is the only sulfide and bismite, Bi_2O_3, is the only oxide, of bismuth; both are to be found in this part of the S_2–O_2 field.

Entropy data for $Bi_2(SO_4)_3$ are not available. In order to complete the



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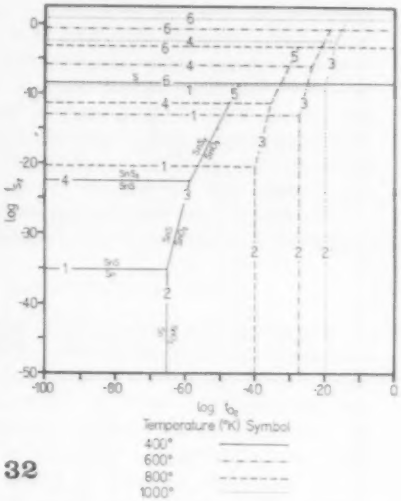

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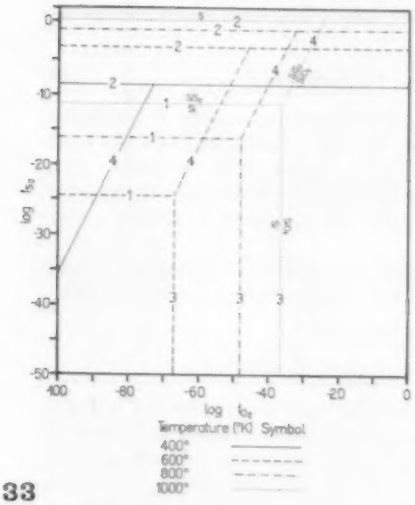

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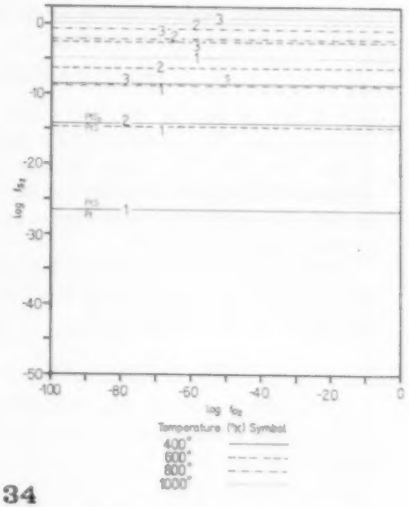

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FIG. 31. Projection of the log fo_2–log fs_2–T diagram for the Ti–O–S system on the basal plane.

FIG. 32. Projection of the log fo_2–log fs_2–T diagram for the Sn–O–S system on the basal plane.

FIG. 33. Projection of the log fo_2–log fs_2–T diagram for the Si–O–S system on the basal plane.

FIG. 34. Projection of the log fo_2–log fs_2–T diagram for the Pt–O–S system on the basal plane.

diagram the value of 57.2 cal/deg-mol was assigned to the entropy of this compound. This is the value of the entropy at 298° K of $Al_2(SO_4)_3$. No estimate of the uncertainty in the assigned value can be given but it is probably less than 10 cal/deg-mol as can be seen by the similarity of the entropy of series of compounds of similar formula type. In the relationship of sulfate to oxide and native metal, bismuth occupies a position intermediate between that of metals such as silver and mercury on the one hand and manganese, zinc and iron on the other.

No data are available on bismuth carbonates, and no anhydrous bismuth carbonate has been reported as a mineral.

THE STABILITY FIELD OF ANTIMONY MINERALS

Figure 30 shows the stability fields of antimony and of some of its compounds in S_2–O_2–T projection. The native metal, stibnite, Sb_2S_3, senarmontite and valentinite, Sb_2O_3, kermesite, Sb_2S_2O, and the sulfate $Sb_2(SO_4)_3$, are represented at 400° K. Stibiconite, SbO_2, and Sb_2O_5 appear in this portion of the S_2–O_2 field only at 600° K and at higher temperatures. No data for the compound Sb_2S_5 are available.

Considerable uncertainty remains about the position of the kermesite and $Sb_2(SO_4)_3$ fields. No thermodynamic data are available for kermesite. In calculating the position of its stability field it has been assumed that the enthalpy change in the reaction

$$[Sb_2O_3] + 2[Sb_2S_3] \rightarrow 3[Sb_2S_2O] \qquad (18)$$

is 5 Kcal per mol of $[Sb_2S_2O]$ and that the entropy change is negligible. The enthalpy change assumed for the reaction may be appreciably too large. If this is so, the kermesite field as shown in Figure 30 is too wide. It is doubtful that neglecting the entropy change causes any appreciable error, so that the kermesite field almost certainly will be found to occupy a strip in the position indicated.

The entropy value for $Sb_2(SO_4)_3$ is similarly lacking. The same expedient was used as in the case of $Bi_2(SO_4)_3$, i.e., the entropy value for $Al_2(SO_4)_3$ was used in the calculations.

THE STABILITY FIELDS OF TITANIUM MINERALS

Three titanium sulfides: TiS, TiS_2 and TiS_3 and four oxides, TiO, Ti_2O_3, Ti_3O_5, and TiO_2 are known, and their relationships are shown in Figure 31. No data are available for carbonates or sulfates of titanium. The diagram in Figure 31 is unique in that the whole of the geologically significant portion lies to the right of the Ti_3O_5–TiO_2 boundary. No sulfides of titanium are therefore to be expected to occur as minerals, which is indeed the case.

THE STABILITY FIELDS OF TIN MINERALS

Figure 32 shows the relationships in the S_2–O_2–T diagram for native tin, cassiterite, SnO_2, herzenbergite, SnS, and the disulfide, SnS_2. Unfortunately no data are available for stannite, for other sulfide minerals containing tin, or for sulfates or carbonates of tin.

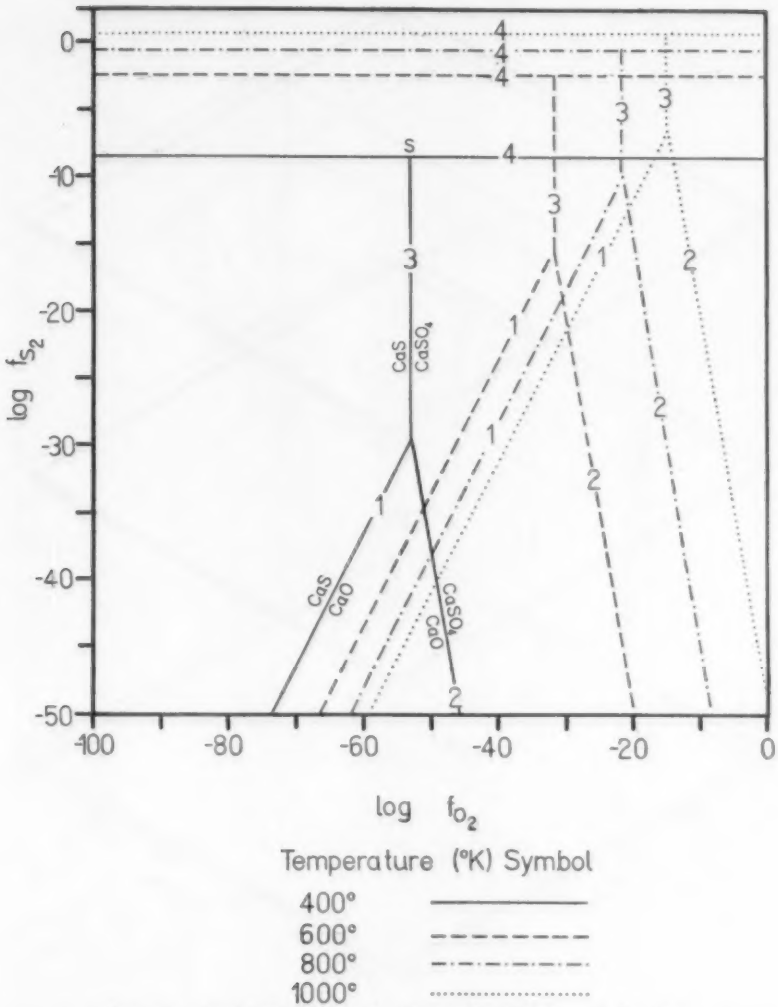


FIG. 35. Projection of the log fo_2–log fs_2–T diagram for the Ca–O–S system on the basal plane.

THE STABILITY FIELDS OF SILICON MINERALS

The stability fields of Si, SiS_2 and SiO_2 as shown in Figure 33 are similar to those of the corresponding tin minerals. However no stable monosulfide corresponding to herzenbergite occurs. Since neither native silicon nor SiS_2 occur as minerals, the left boundary of the SiO_2 field is geologically significant.

No data are available for sulfates or carbonates of silicon.

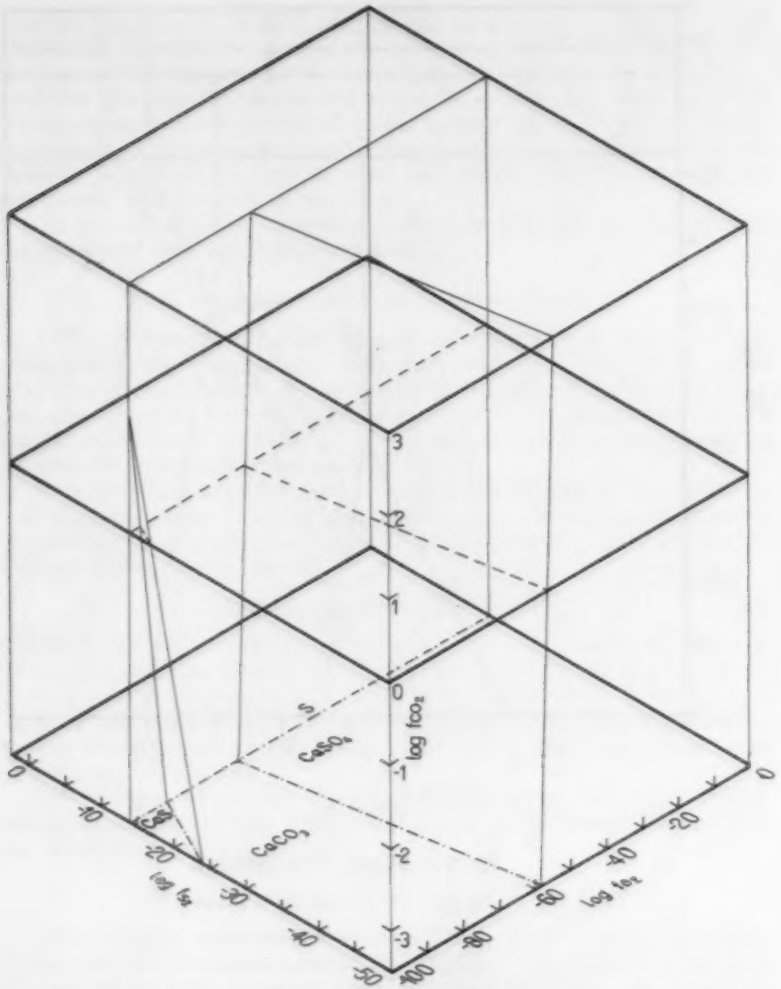


FIG. 36. The log fo_2–log fs_2–log fco_2 diagram for the Ca–O–S–C system at 300° K.

THE STABILITY FIELDS OF PLATINUM MINERALS

No oxides, sulfates, or carbonates of platinum occur as minerals. The native metal, and the monosulfide, cooperite, PtS, have been found associated, but the disulfide, PtS_2, seems not to have been recorded. The diagram of Figure 34 is thus very simple, containing only the fields of the metal and of the two sulfides.

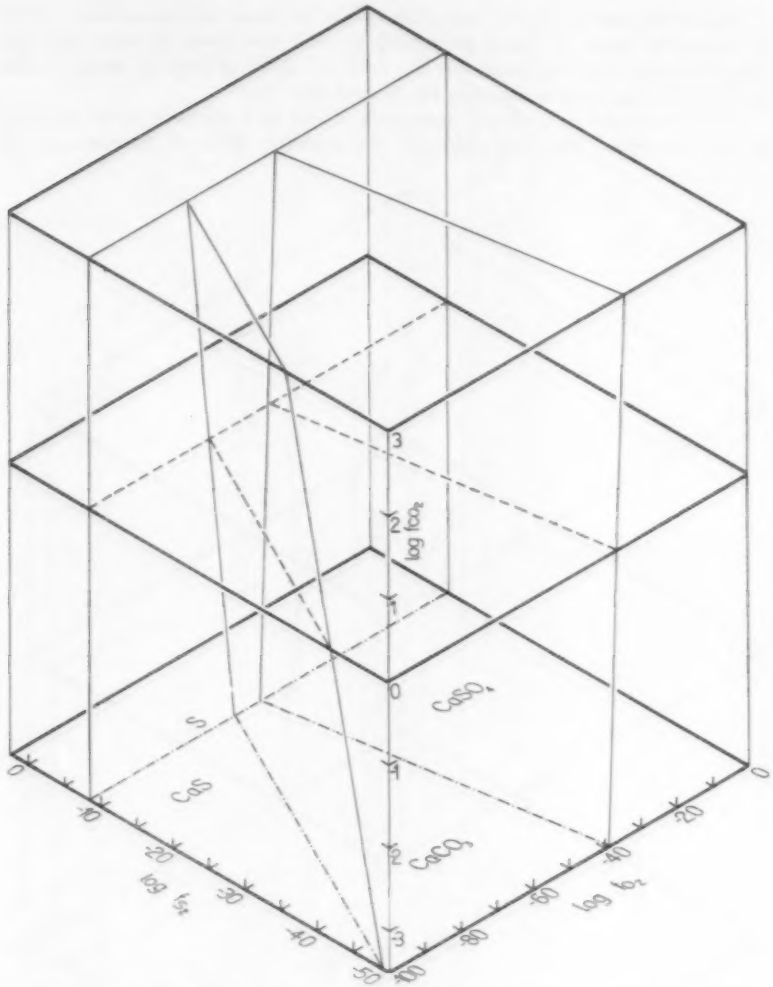


FIG. 37. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Ca–O–S–C system at 400° K.

THE STABILITY FIELDS OF CALCIUM MINERALS

Even at 1,000° K the stability field of calcium metal does not appear in the diagram of Figure 35. Oldhamite, CaS, is the only sulfide of calcium, and CaO the only oxide in the diagram. The dioxide, CaO_2, is stable only at O_2 pressures in excess of one atmosphere at room temperature. Anhydrite, $CaSO_4$, takes up the remainder of the diagram.

Since the free energy of formation of $CaCO_3$ from the constituent oxides is relatively large, it is not surprising to find that even at very low CO_2 fugacities and high temperatures the field of $CaCO_3$ is large as shown in the S_2–O_2–CO_2 diagrams of Figures 36, 37 and 38.

Calcium is the only metal commonly found as a primary halide mineral in ore deposits. The discussion of the stability field of fluorite and its

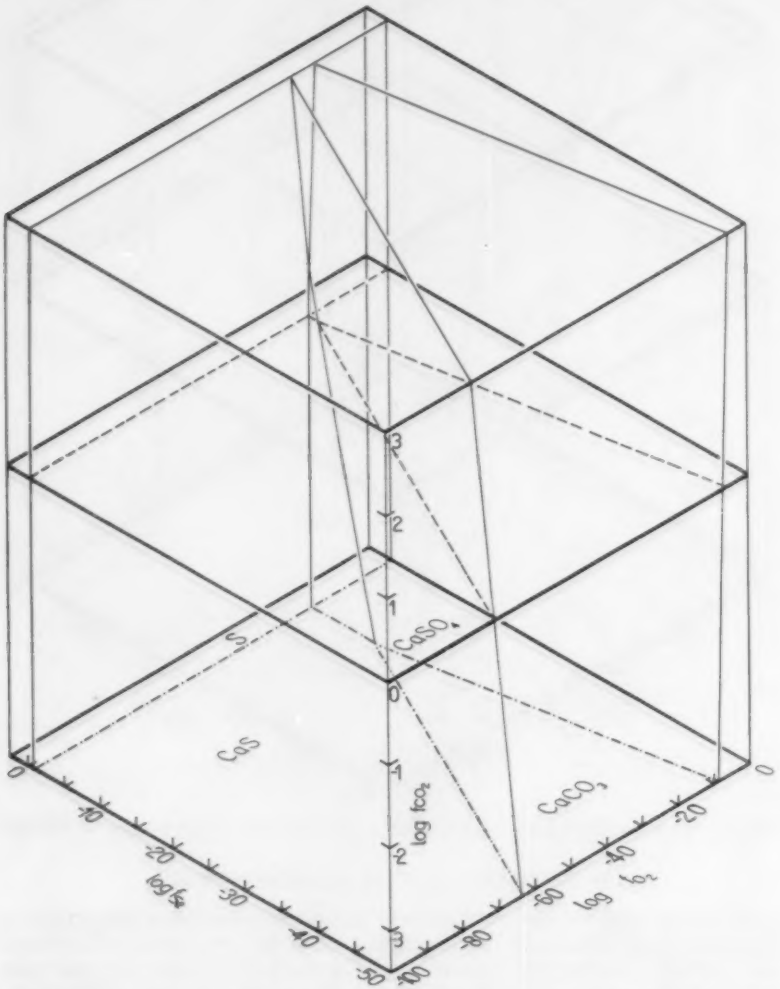


FIG. 38. The log fo_2–log fs_2–log fco_2 diagram for the Ca–O–S–C system at 800° K.

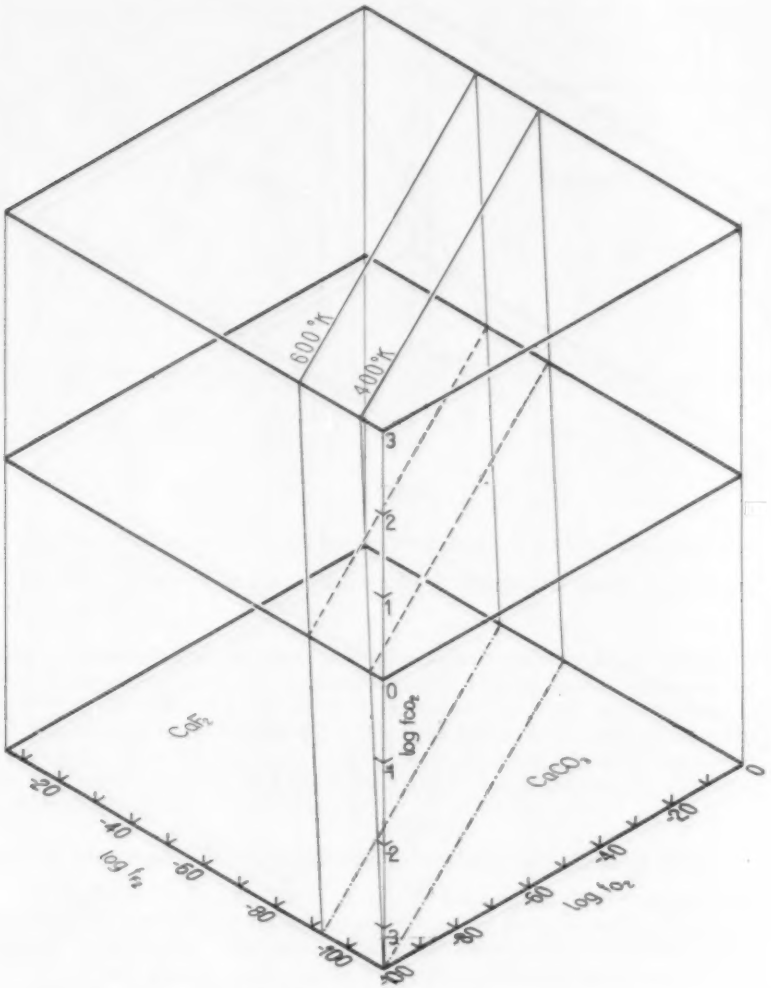


FIG. 39. The log f_{O_2}–log f_{F_2}–log f_{CO_2} diagram for the Ca–O–F–C system at 400 and 600° K.

relationship to other calcium minerals is thus of particular importance since the occurrence of fluorite, or of calcite or of both of these minerals together yields information concerning the fugacity of fluorine in the ore forming fluid at the time of deposition of the vein minerals. A logical extension of the treatment up to this point would be the discussion of calcium minerals in

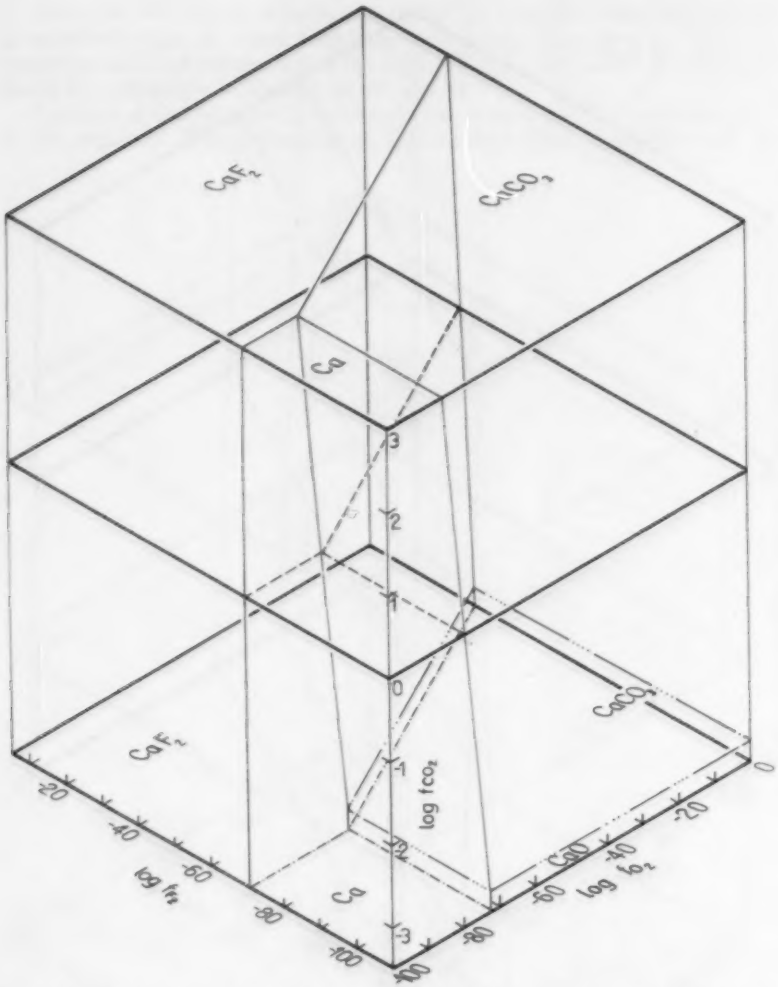
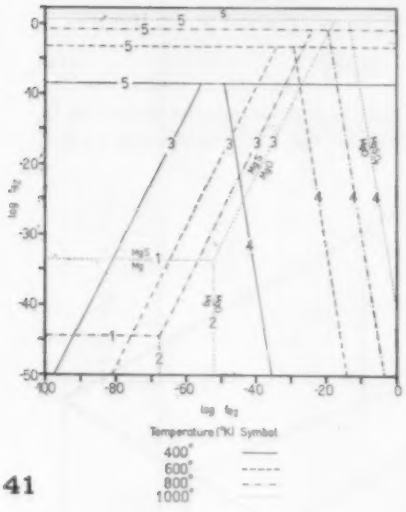


FIG. 40. The log f_{O_2}–log f_{F_2}–log f_{CO_2} diagram for the system Ca–O–F–C at 800° K.

S_2–O_2–CO_2–F_2 space. This would be cumbersome, and since the sulfur compounds of calcium are only rarely found in ore deposits, the Ca–O_2–F_2–CO_2 portion of the Ca–O_2–S_2–CO_2–F_2 system is here considered. The resulting isothermal diagrams at 400° K, 600° K and 800° K are shown in Figures 39 and 40. At 400° K and 600° K calcite and fluorite are the only calcium compounds present in the portion of the diagram shown in Figure 39. The



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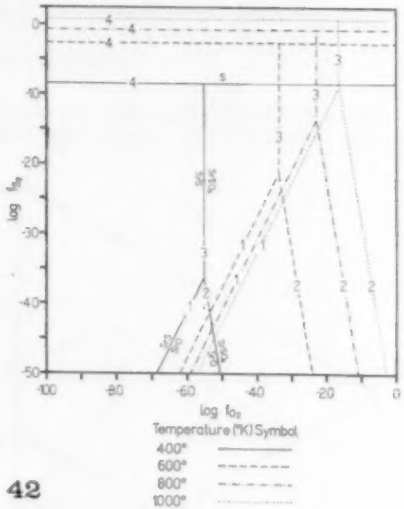

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FIG. 41. Projection of the log fo_2–log fs_2–T diagram for the Mg–O–S system on the basal plane.

FIG. 42. Projection of the log fo_2–log fs_2–T diagram for the Sr–O–S system on the basal plane.

fields of these minerals are separated by a slightly inclined plane that shifts towards higher values of the fluorine fugacity with increasing temperature. At 800° K the fields of both CaO and native calcium occur in the portion of the diagram shown in Figure 40. The right hand portion of this diagram contains the plane of the CaF_2–$CaCO_3$ boundary; the left front portion of the diagram is similar to the relationships observed in S_2–O_2–CO_2 diagrams previously discussed.

THE STABILITY FIELDS OF MAGNESIUM, STRONTIUM AND BARIUM MINERALS

As might be expected, the diagrams of Figures 41–45 for magnesium, strontium and barium compounds are very similar to the corresponding ones for calcium minerals. The position of the stability fields of the magnesium, strontium and barium compounds is slightly different from that of the calcium minerals, and these differences are useful in defining the conditions prevailing during ore deposition, particularly where barium is present as the sulfate, barite, while calcium is present as the carbonate, calcite, as pointed out by Barton (1a).

THE STABILITY FIELD OF CARBON

Graphite is the stable form of carbon at pressures and temperatures characteristic of ore deposition. When graphite is present, the ratio of the

fugacity of oxygen to that of CO_2 is fixed by equilibrium in the reaction

$$[C] + (O_2) \rightarrow (CO_2). \tag{19}$$

In the S_2–O_2–CO_2 diagrams equation 19 defines a plane parallel to the log f_{S_2} axis. At any given temperature and value of the CO_2 fugacity this plane

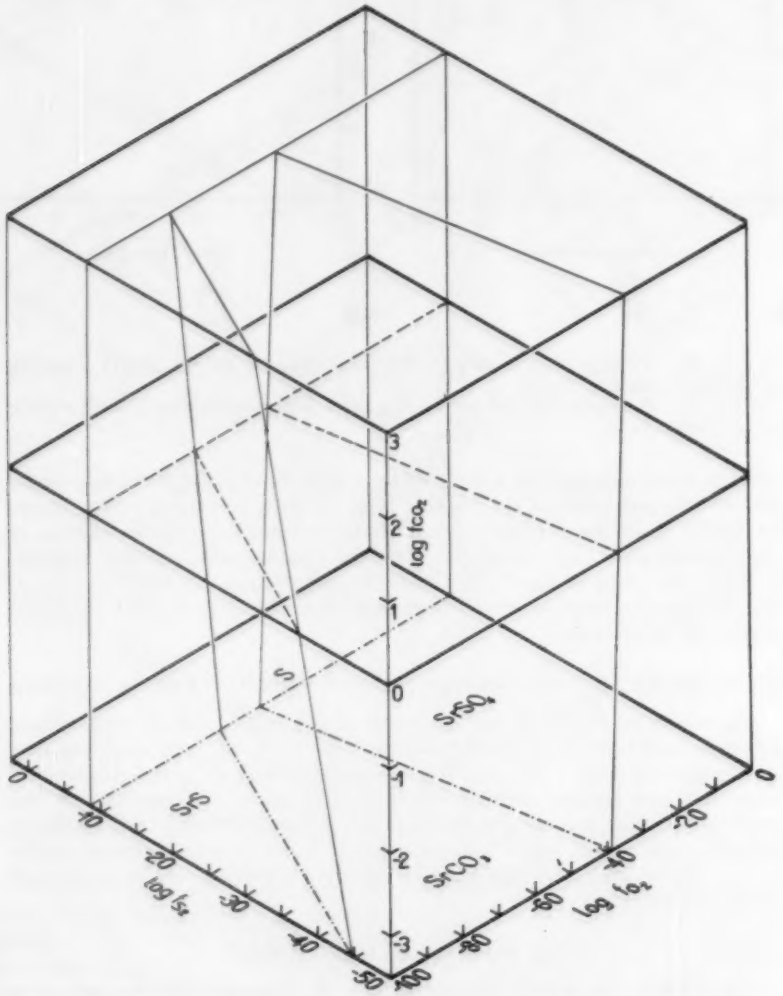

FIG. 43. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the Sr-O-S-C system at 400° K.

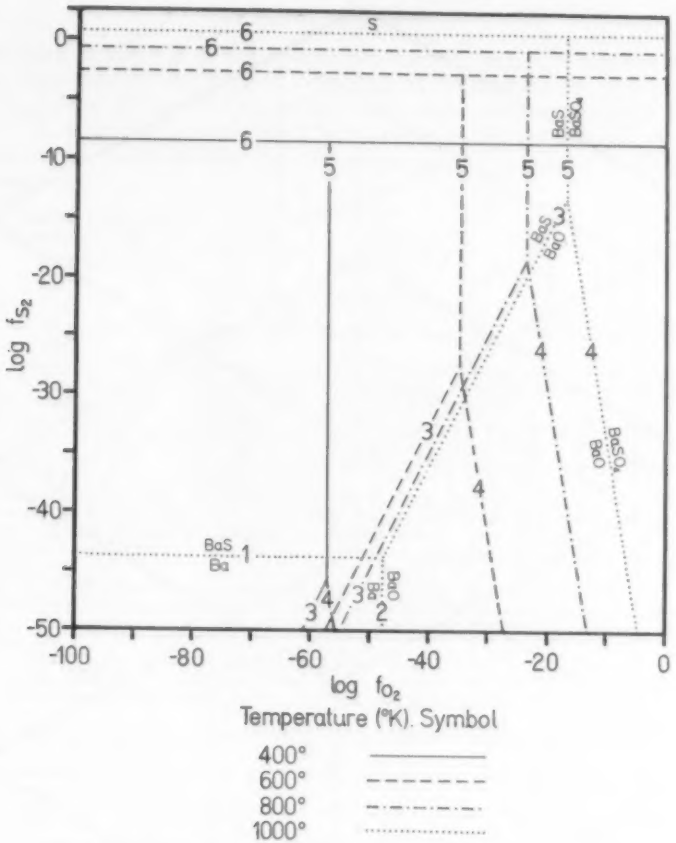

FIG. 44. Projection of the log fo_2–log fs_2–T diagram for the Ba–O–S system on the basal plane.

determines the minimum value of the oxygen fugacity since an extraction of O_2 from the system results in the decomposition of CO_2 into graphite and oxygen until the oxygen fugacity again reaches the required level.

CONCLUDING REMARKS

The diagrams developed in this paper possess a basic similarity but differ a good deal in the size, shape and position of the stability fields of the various compounds of the respective elements. Thus, if we pick a point in S_2–O_2–CO_2 space at a given temperature, we may be in the field of stability of one of the oxides of one element, in that of a sulfide of a second, in that of

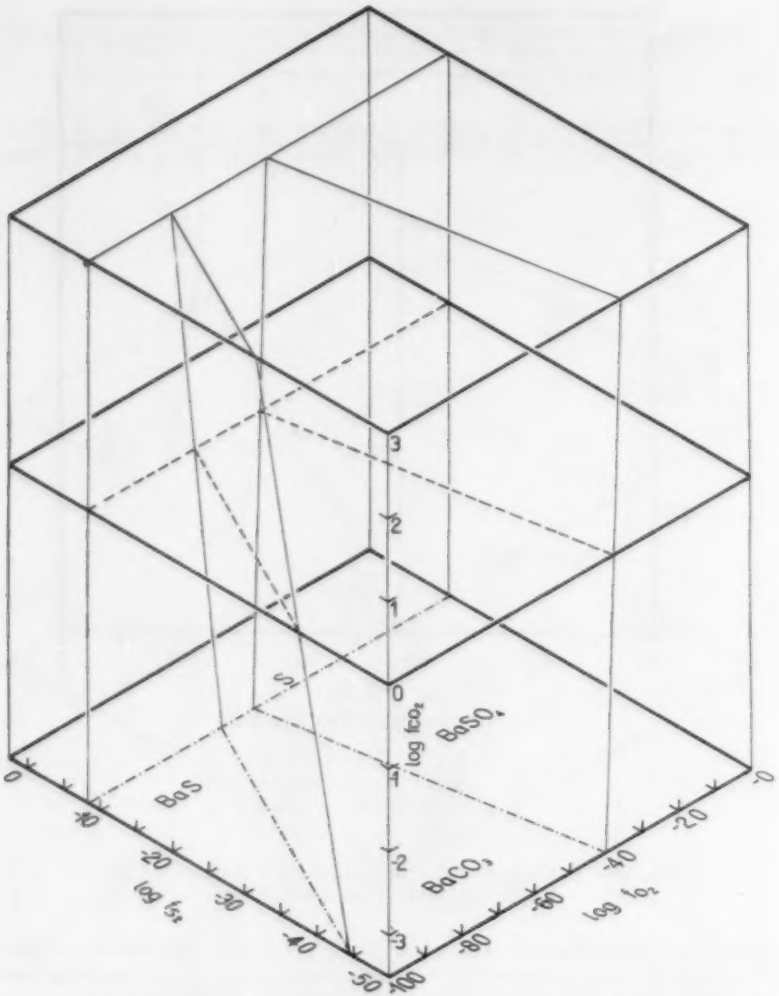

FIG. 45. The log f_{O_2}–log f_{S_2}–log f_{CO_2} diagram for the system Ba–O–S–C at 400° K.

a carbonate of a third, of a sulfate of a fourth, and of the native element in the case of a fifth element. During ore deposition such a variety of chemical combinations is commonly observed, and it is the task of the second of these papers to relate and interpret the observed associations in terms of the diagrams of the respective metals in S_2–O_2–CO_2 space at the appropriate temperatures.

ACKNOWLEDGMENTS

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PRINCETON, N. J.,
May 6, 1958

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APPENDIX

Reaction	A	B	C	±, Kcal	Temp. range (° K)	Source	Comments
(1) *Iron*							
$2[Fe]_{\alpha} + (S_2) \rightarrow 2[FeS]_{\alpha}$	−74,320		31.18	1	298 to 412	(9) Table E	
$2[Fe]_{\alpha} + (S_2) \rightarrow 2[FeS]_{\beta}$	−71,820		25.12	1	412 to 1,179	(9) Table E	
$2[Fe]_{\gamma} + (S_2) \rightarrow 2[FeS]_{\beta}$	−72,140		25.48	2	1,179 to 1,261	(9) Table E	good agreement with K + C values (10)
$2[\overline{FeS}] + (S_2) \rightarrow 2[\overline{FeS_2}]$	−86,700		90.0	3	298 to 1,100	(9) Table E	extrapolated down to 298°; in good agreement with R + J (12) but not with K + C (10)
$1.9[Fe] + (O_2) \rightarrow 2[Fe_{0.95}O]$	−126,360		33.35	3(?)	833 to 1,200	(10)	good agreement with K + E, table E (9)
$6[\overline{FeO}] + (O_2) \rightarrow 2[Fe_3O_4]$	−149,300		59.50		833 to 1,200	(10)	
$\frac{3}{2}[Fe]_{\alpha} + (O_2) \rightarrow \frac{1}{2}[Fe_3O_4]_{\alpha}$	−133,900		41.10	1	298 to 833	(10)	
$4[Fe_3O_4] + (O_2) \rightarrow 6[Fe_2O_3]$	−119,200		67.2	5	300 to 1,200	(10)	
$3[Fe_2SiO_4] + (O_2) \rightarrow 2[Fe_3O_4] + 3[SiO_2]$	−127,000		48.6	5(?)	300 to 1,500	(18)	good agreement on A with K + E, table A, but poor with B from same source
$[FeS_2] + 2(O_2) \rightarrow [FeSO_4] + \frac{1}{2}(S_2)$	−162,600		57.8	8	300 to 1,000	(9) Table A	
$[Fe_2O_3] + (S_2) + \frac{5}{2}(O_2) \rightarrow 2[FeSO_4]$	−275,000		147.1	14	300 to 1,000	(9) Table A	
$[Fe] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [FeCO_3]$	−84,700		60.1	3	300 to 1,000	(9) Table A	
$[Fe_3O_4] + 3(CO_2) \rightarrow 3[FeCO_3] + \frac{1}{2}(O_2)$	+14,000		97.2	12	300 to 1,000	(9) Table A	
$[Fe_2O_3] + 2(CO_2) \rightarrow 2[FeCO_3] + \frac{1}{2}(O_2)$	+27,700		54.8	8	300 to 1,000	(9) Table A	
$[FeS] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [FeCO_3] + \frac{1}{2}(S_2)$	−46,350		42.3	4	300 to 1,000	(9) Table A	
$[FeS_2] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [FeCO_3] + (S_2)$	−11,350		11.7	6	300 to 1,000	(9) Table A	
$[FeSO_4] + (CO_2) \rightarrow [FeCO_3] + \frac{1}{2}(S_2) + \frac{1}{2}(O_2)$	151,300		−46.1	10	300 to 1,000	(9) Table A	
$[FeS] + 2(O_2) \rightarrow [FeSO_4]$	−197,700		88.4	7	300 to 1,000	(9) Table A	
(2) *Manganese*							
$2[Mn]_{\alpha} + (S_2) \rightarrow 2[MnS]$	−128,000		30.64	3	298 to 1,000	(9) Table E	good agreement with data from K + E, Table A
$2[Mn] + (O_2) \rightarrow 2[MnO]$	−183,900		34.8	6	298 to 1,500	(9) K + E, Table E	good agreement with K + C, R + J (12) and K + E, Table A

APPENDIX—*Continued*

Reaction	A	B	C	± Kcal	Temp. range (° K)	Source	Comments
$6[MnO] + (O_2) \rightarrow 2[Mn_3O_4]$	−110,800		63.8	4	300 to 1,000	(9) Table A	poor agreement with calculation based on K + C data
$4[Mn_3O_4] + (O_2) \rightarrow 6[Mn_2O_3]$	−50,800		32.6	20	300 to 1,000	(9) Table A	fair agreement with K + C data for 800° to 1,400° K
$2[Mn_2O_3] + (O_2) \rightarrow 4[MnO_2]$	−38,400		51.0	6	300 to 1,000	(9) Table A	fair agreement with K + C data for 800° to 1,400° K
$[MnS] + 2(O_2) \rightarrow [MnSO_4]$	−205,200		89.9	2	300 to 1,000	(9) Table A	
$[MnO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [MnSO_4]$	−177,700		88.2	3	300 to 1,000	(9) Table A	
$[Mn_3O_4] + \frac{3}{2}(S_2) + 4(O_2) \rightarrow 3[MnSO_4]$	−477,700		232.7	7	300 to 1,000	(9) Table A	
$[Mn_2O_3] + (S_2) + \frac{5}{2}(O_2) \rightarrow 2[MnSO_4]$	−310,000		149.7	6	300 to 1,000	(9) Table A	
$[MnO_2] + \frac{1}{2}(S_2) + (O_2) \rightarrow [MnSO_4]$	−145,400		62.1	3	300 to 1,000	(9) Table A	
$[MnO] + (CO_2) \rightarrow [MnCO_3]$	−26,250		40.5		300 to 1,000	Goldsmith and Graf (5)	fair agreement with data from K + E, Table A
$[MnS] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [MnCO_3] + \frac{1}{2}(S_2)$	−55,400		46.6	3	300 to 1,000	K + E, Table A	
$[MnSO_4] + (CO_2) \rightarrow [MnCO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2)$	149,800		−43.3	3	300 to 1,000	K + E, Table A	
$[MnCO_3] + [SiO_2] \rightarrow [MnSiO_3] + (CO_2)$	21,980		−41.9	6	300 to 1,000	Goldsmith and Craf (5) and K + E, Table E	not good agreement with data from Table A
$[MnSiO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [MnSO_4] + [SiO_2]$	−171,780		85.2	6	300 to 1,000	(9) Table A and Table E	
$[MnS] + [SiO_2] + \frac{1}{2}(O_2) \rightarrow [MnSiO_3] + \frac{1}{2}(S_2)$	−33,870		5.1	6	300 to 1,000	(9) Table E	
(3) *Lead*							
$2[Pb] + (S_2) \rightarrow 2[PbS]$	−145,420		68.3	3	298 to 600	(9) Table E	
$2[Pb] + (S_2) \rightarrow 2[PbS]$	−150,320		76.5	3	600 to 1,380	(9) Table E	
$2[Pb] + (O_2) \rightarrow 2[PbO]$	−105,700	−6.90	67.6	2	298 to 600	(9) Table E	
$2[Pb] + (O_2) \rightarrow 2[PbO]$	−109,900	−16.1	100.2	3	600 to 1,150	(9) Table E	
$[PbS] + 2(O_2) \rightarrow [PbSO_4]$	−197,000		84.6	3	300 to 1,000	(9) Table A	
$[PbO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [PbSO_4]$	−182,600		81.7	3	300 to 1,000	(9) Table A	
$3[PbO] + \frac{1}{2}(O_2) \rightarrow [Pb_3O_4]$	−18,600		22.6	8	300 to 1,000	(9) Table A	
$[PbS] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [PbCO_3] + \frac{1}{2}(S_2)$	−35,300		38.9	5	300 to 1,000	(9) Table A	

APPENDIX—*Continued*

Reaction	A	B	C	± Kcal	Temp. range (° K)	Source	Comments
$[PbSO_4] + (CO_2) \rightarrow [PbCO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2)$	+161,700		−45.7	5	300 to 1,000	(9) Table A	
$[Pb] + \frac{1}{2}(O_2) + (CO_2) \rightarrow [PbCO_3]$	−73,300		59.8	3	300 to 1,000	(9) Table A	
$[PbO] + (CO_2) \rightarrow [PbCO_3]$	−20,900		36.0	4	300 to 1,000	(9) Table A	
(4) *Zinc*							
$2[Zn] + (S_2) \rightarrow 2[ZnS]$	−127,300	−9.2	73.4	8	298 to 693	(9) Table E	
$2[Zn] + (S_2) \rightarrow 2[ZnS]$	−189,940	−16.1	149.8	10	693 to 1,200	(9) Table E	
$2[Zn] + (O_2) \rightarrow 2[ZnO]$	−168,200	−13.8	88.3	3	298 to 693	(9) Table E	
$2[Zn] + (O_2) \rightarrow 2[ZnO]$	−230,840	−20.7	164.8	4	693 to 1,200	(9) Table E	
$[ZnS] + 2(O_2) \rightarrow [ZnSO_4]$	−185,700		81.2	7	300 to 1,000	(9) Table A	
$[ZnO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [ZnSO_4]$	−166,200		80.5	5	300 to 1,000	(9) Table A	
$[ZnO] + (CO_2) \rightarrow [ZnCO_3]$	−17,000		41.8	1	300 to 1,000	(9) Table A	poor agreement with data of Harker and Hutta (6). The data shown are preferred since value for C is consistent with that for other carbonates
$[ZnS] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [ZnCO_3] + \frac{1}{2}(S_2)$	−36,500		42.5	4	300 to 1,000	(9) Table A	
$[ZnSO_4] + (CO_2) \rightarrow [ZnCO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2)$	149,200		−38.7	6	300 to 1,000	(9) Table A	
$2[ZnO] + [SiO_2] \rightarrow [Zn_2SiO_4]$	−7,130		0.23	2	300 to 1,300	(9) Table E	
(5) *Copper*							
$4[Cu] + (S_2) \rightarrow 2[Cu_2S]_\alpha$	−71,310	−8.68	54.6	2	298 to 376	(10)	good agreement with data of K + E, Table E
$4[Cu] + (S_2) \rightarrow 2[Cu_2S]_\beta$	−71,280		90.96	2	376 to 623	(9) Table E	
$4[Cu] + (S_2) \rightarrow 2[Cu_2S]_\gamma$	−67,240	−22.70 −9.2	46.7	2	623 to 1,383	(9) Table E	excellent agreement with data of K + C
$\frac{1}{2}[Cu_9S_5] + (S_2) \rightarrow 9/2[CuS]$	−42,960		48.5	1.5	298 to 376	(9) Table E	these data are listed for the reaction $2[Cu_2S] + [S_2] - 4[CuS]$ which is unlikely since digenite is a stable intermediate phase

APPENDIX—*Continued*

Reaction	A	B	C	± Kcal	Temp. range (° K)	Source	Comments
$\frac{1}{2}[Cu_2S_2] + (S_2) \rightarrow 9/2[CuS]$	−44,800		53.4	1.5	376 to 623	(9) Table E	
$\frac{1}{2}[Cu_2S_2] + (S_2) \rightarrow 9/2[CuS]$	−45,200		54.00	1.5	623 to 900	(9) Table E	
$4[Cu] + (O_2) \rightarrow 2[Cu_2O]$	−81,000	−7.84	59.0	2	298 to 1,356	(9) Table E	good agreement with R + J (12) data
$2[Cu_2O] + (O_2) \rightarrow 4[CuO]$	−69,900	−12.2	88.3	1	298 to 1,300	(9) Table E	
$[Cu_2S] + 2(O_2) \rightarrow [Cu_2SO_4]$	−177,600		78.6	ca. 10	300 to 1,000	(9) Table A	
$2[CuS] + 2(O_2) \rightarrow [Cu_2SO_4] + \frac{1}{2}(S_2)$	−157,500		54.7	ca. 10	300 to 1,000	(9) Table A	
$[Cu_2O] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [Cu_2SO_4]$	−182,700		76.2	ca. 9	300 to 1,000	(9) Table A	
$2[CuO] + \frac{1}{2}(S_2) + (O_2) \rightarrow [Cu_2SO_4]$	−138,500		48.7	ca. 10	300 to 1,000	(9) Table A	
$[Cu_2SO_4] + \frac{1}{2}(S_2) + 2(O_2) \rightarrow 2[CuSO_4]$	−186,300		122.5	ca. 15	300 to 1,000	(9) Table A	
(6) *Nickel*							
$3[Ni] + (S_2) \rightarrow [Ni_3S_2]$	−79,240		39.01	2	650 to 800	(9) Table E	
$4[Ni_3S_2] + (S_2) \rightarrow 2[Ni_6S_4]$	−49,260		19.91	ca. 3	up to 798	Rosenqvist (14)	
$2[Ni_6S_4] + (S_2) \rightarrow 12[NiS]$	−53,600		30.53	ca. 3		Rosenqvist (14)	
$2[NiS_{1+x}] + (S_2) \rightarrow 2[NiS_2]$	−52,560		50.29	ca. 3	above 600	Rosenqvist (14)	
$2[Ni] + (O_2) \rightarrow 2[NiO]$	−116,900		47.10	4	298 to 1,725	(9) Table E	
$2[NiO] + (S_2) + 3(O_2) \rightarrow 2[NiSO_4]$	−341,000		173.4	15	300 to 1,000	(9) Table A	
(7) *Cobalt*							
$\frac{3}{4}[Co] + (S_2) \rightarrow \frac{1}{4}[Co_3S_4]$	−79,240		39.81	2	298 ca. to 1,048	(9) Table E	
$8/3[Co] + (S_2) \rightarrow \frac{2}{3}[Co_4S_{2-x}]$	−61,900		23.29		ca. 1,048 to ca. 1,205	Rosenqvist (14)	
$2[Co] + (S_2) \rightarrow 2[CoS]$	−72,060		33.73		733 to m.p. of CoS	Rosenqvist (14)	
$\frac{3}{4}[Co_3S_4] + (S_2) \rightarrow \frac{3}{4}[Co_2S_4]$	−51,640		34.03		298 to 733	Rosenqvist (14)	
$[Co_3S_4] + (S_2) \rightarrow 3[CoS_2]$	−50,160		50.41	3	600 to 900	Rosenqvist (14)	
$2[Co_3S_4] + (S_2) \rightarrow 18[CoS]$	−14,600		−14.9	ca. 6	733 to ca. 1,200	Rosenqvist (14)	
$6[CoS] + (S_2) \rightarrow 2[Co_3S_4]$	−63,980		50.3		733 to 900	Rosenqvist (14)	
$2[CoS] + (S_2) \rightarrow 2[CoS_2]$	−54,770		50.4		above 900	Rosenqvist (14)	
$2[Co] + (O_2) \rightarrow 2[CoO]$	−113,900		37.1	6	298 to 1,300	(9) Table E	
$3[CoO] + \frac{1}{2}(O_2) \rightarrow [Co_3O_4]$	−38,870	−0.95	33.87	2	298 to 1,300	(9) Table E	
$[CoO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [CoSO_4]$	−165,800		87.0	10	300 to 1,000	(9) Table A	
$2[Co_3O_4] + 3(S_2) + 8(O_2) \rightarrow 6[CoSO_4]$	−917,060	+1.90	454.3	64	300 to 1,000	(9) Table A	

APPENDIX—*Continued*

Reaction	A	B	C	± Kcal	Temp. range (° K)	Source	Comments
(8) *Mercury*							
$2[Hg] + (S_2) \rightarrow 2[HgS]$	−58,800		51.8	7	300 to 600	(9) Table A	
$2[Hg] + (O_2) \rightarrow 2[HgO]$	−43,400		51.8	1	300 to 600	(9) Table A	
$2[HgS] + 2(O_2) \rightarrow [Hg_2SO_4] + \frac{1}{2}(S_2)$	−134,000		61.8	11	300 to 600	(9) Table A	
$2[HgO] + \frac{1}{2}(S_2) + (O_2) \rightarrow [Hg_2SO_4]$	−149,400		61.8	7	300 to 600	(9) Table A	
$2[Hg] + \frac{1}{2}(S_2) + 2(O_2) \rightarrow [Hg_2SO_4]$	−192,800		113.6	6	300 to 600	(9) Table A	
$[Hg_2SO_4] + \frac{1}{2}(S_2) + 2(O_2) \rightarrow 2[HgSO_4]$	−174,800		115.2	26	300 to 600	(9) Table A	
(9) *Silver*							
$4[Ag] + (S_2) \rightarrow 2[Ag_2S]_\alpha$	−44,800		22.1	1	298 to 452	(9) Table E	
$4[Ag] + (S_2) \rightarrow 2[Ag_2S]_\beta$	−41,980		16.52	1	452 to 1,115	(9) Table E	
$4[Ag] + (O_2) \rightarrow 2[Ag_2O]$	−14,600		31.6	1	300 to 1,000	(9) Table A	
$2[Ag] + \frac{1}{2}(S_2) + 2(O_2) \rightarrow [Ag_2SO_4]$	−186,000		97.7	3	300 to 1,000	(9) Table A	
$[Ag_2S] + 2(O_2) \rightarrow [Ag_2SO_4]$	−163,000		84.8	3	300 to 1,000	(9) Table A	
(10) *Bismuth*							
$2[Bi] + \frac{3}{2}(S_2) \rightarrow [Bi_2S_3]$	−84,810	−16.86	112.9	3	298 to 544	(9) Table E	fair agreement with data from Table A. The data are used here up to 1,000° K
$2[Bi] + \frac{3}{2}(O_2) \rightarrow [Bi_2O_3]$	−138,000		64.5	5	298 to 544	(9) Table A	
$2[Bi] + \frac{3}{2}(S_2) + 6(O_2) \rightarrow [Bi_2(SO_4)_3]$	−653,500		345.6	15	298 to 544	(9) Table A	
$[Bi_2S_3] + 6(O_2) \rightarrow [Bi_2(SO_4)_3]$	−564,800		274.0	15	300 to 1,000	(9) Table A	
$[Bi_2O_3] + \frac{3}{2}(S_2) + 9/2(O_2) \rightarrow [Bi_2(SO_4)_3]$	−515,500		281.1	18	300 to 1,000	(9) Table A	
(11) *Antimony*							
$2[Sb] + \frac{3}{2}(S_2) \rightarrow [Sb_2S_3]$	−87,000		73.1	9	300 to 1,000	(9) Table A	
$2[Sb] + \frac{3}{2}(O_2) \rightarrow [Sb_2O_3]$	−167,000		65.9	4	300 to 1,000	(9) Table A	
$[Sb_2O_3] + \frac{1}{2}(O_2) \rightarrow 2[SbO_2]$	−25,000		23.5	16	300 to 1,000	(9) Table A	
$2[SbO_2] + \frac{1}{2}(O_2) \rightarrow [Sb_2O_5]$	−23,000		25.0	29	300 to 1,000	(9) Table A	
$[Sb_2O_3] + \frac{3}{2}(S_2) + 9/2(O_2) \rightarrow [Sb_2(SO_4)_3]$	−454,800		274.4	16	300 to 1,000	(9) Table A	
$2[SbO_2] + \frac{3}{2}(S_2) + 4(O_2) \rightarrow [Sb_2(SO_4)_3]$	−429,800		250.8	25	300 to 1,000	(9) Table A	
$2[Sb_2S_3] + [Sb_2O_5] \rightarrow 3[Sb_2S_2O]$	−15,000		0	10	300 to 1,000		estimate on theoretical grounds
$[Sb_2S_3] + \frac{1}{2}(O_2) \rightarrow [Sb_2S_2O] + \frac{1}{2}(S_2)$	−32,000		−2.4	12	300 to 1,000	(9) Table A	used data from above equation as well

APPENDIX—*Continued*

Reaction	A	B	C	± Kcal	Temp. range (°K)	Source	Comments
$[Sb_2S_2O] + (O_2) \rightarrow [Sb_2O_3] + (O_2)$	−48,000		−4.8	9	300 to 1,000	(9) Table A	used data from above equation as well
$2[Sb] + (S_2) + \frac{1}{2}(O_2) \rightarrow [Sb_2S_2O]$	−119,000		70.7	7	300 to 1,000	(9) Table A	used data from above equation as well
$[Sb_2S_3O] + \frac{1}{2}(S_2) + 11/2(O_2) \rightarrow [Sb_2(SO_4)_3]$	−502,800		269.6	16	300 to 800	(9) Table A	used data from above equation as well
$[Sb_2S_3] + 6(O_2) \rightarrow [Sb_2(SO_4)_3]$	−534,800		267.1	18	300 to 1,000	(9) Table A	
(12) *Titanium*							
$['Ti'] + \frac{1}{2}(O_2) \rightarrow ['TiO']$	−122,300		21.3	4	600 to 2,000	(9) Table E	
$2['TiO'] + \frac{1}{2}(O_2) \rightarrow [Ti_2O_3]$	−114,150		19.05	4	298 to 2,000	(9) Table E	
$3[Ti_2O_3] + \frac{1}{2}(O_2) \rightarrow 2[Ti_3O_5]$	−88,500		19.7	3	700 to 2,000	(9) Table E	
$[Ti_3O_5] + \frac{1}{2}(O_2) \rightarrow 3['TiO_2']$	−73,000		23.0	3	298 to 2,123	(9) Table E	
$[Ti] + \frac{1}{2}(S_2) \rightarrow ['TiS']$	−67,500		22.5	10	300 to 1,000	(9) Table A	
$['TiS'] + \frac{1}{2}(S_2) \rightarrow [TiS_2]$	−43,500		20.5	10	300 to 1,000	(9) Table A	
$2[TiS_2] + (S_2) \rightarrow 2['TiS_2']$	−37,200		42.2	ca. 10	300 to 1,000	(10)	
$['TiS'] + \frac{1}{2}(S_2) \rightarrow [TiS_2]$	−43,500		20.5	10	300 to 1,000	(10)	
$2[TiS_2] + (S_2) \rightarrow 2['TiS_2']$	−37,200		42.2	ca. 10	300 to 1,000	(10)	
$2[TiS_2] + \frac{3}{2}(O_2) \rightarrow [Ti_2O_3] + 2(S_2)$	−140,900		−16.6	ca. 8	300 to 1,000	(9) Table A	
$2[TiS] + \frac{3}{2}(O_2) \rightarrow [Ti_2O_3] + (S_2)$	−227,900		24.3	ca. 10	300 to 1,000	(9) Table A	
$2[TiS_2] + \frac{5}{2}(O_2) \rightarrow [Ti_2O_5] + 3(S_2)$	−253,900		−15.4	ca. 10	300 to 1,000	(9) Table A	
$3[TiS_2] + \frac{9}{2}(O_2) \rightarrow [Ti_3O_5] + 9/2(S_2)$	−198,100		−78.8	ca. 10	300 to 1,000	(9) Table A	
(13) *Tin*							
$[Sn] + (O_2) \rightarrow [SnO_2]$	−138,800		48.8	1	300 to 1,000	(9) Table A	
$[Sn] + \frac{1}{2}(S_2) \rightarrow [SnS]$	−40,600		21.1	2	300 to 1,000	(9) Table A	
$[SnS] + \frac{1}{2}(S_2) \rightarrow [SnS_2]$	−30,400		24.7	6	300 to 1,000	(9) Table A	
(14) *Silicon*							
$[Si] + (O_2) \rightarrow [SiO_2]$	−210,600	−3.0	52.22	3	298 to 1,700	(9) Table E	
$[Si] + (S_2) \rightarrow [SiS_2]$	−91,000		39.7	ca. 8	300 to 1,000	(9) Table A	
$[SiO_2] + (S_2) \rightarrow [SiS_2] + (O_2)$	119,600	3.0	−12.5	ca. 10	300 to 1,000	(9) Table E and Table A	
(15) *Platinum*							
$2[Pt] + (S_2) \rightarrow 2[PtS]$	−66,100		43.6	5	1,000 to 1,700	(9) Table E	
$2[PtS] + (S_2) \rightarrow 2[PtS_2]$	−43,750		43.8	5	700 to 1,000	(9) Table E	

APPENDIX—*Continued*

Reaction	A	B	C	± Kcal	Temp. range (° K)	Source	Comments
(16) *Calcium*							
$2[Ca] + (O_2) \rightarrow 2[CaO]$	−302,650		47.32	3	298 to 1,124	(9) Table E	
$2[Ca]_\alpha + (S_2) \rightarrow 2[CaS]$	−258,870		45.62	2	298 to 673	(9) Table E	
$2[Ca]_\beta + (S_2) \rightarrow 2[CaS]$	−259,100		45.92	2	673 to 1,124	(9) Table E	
$[CaS] + 2(O_2) \rightarrow [CaSO_4]$	−232,400		86.0	7	300 to 1,000	(9) Table A	
$[CaO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [CaSO_4]$	−206,000		84.7	5	300 to 1,000	(9) Table A	
$2[CaO] + (S_2) \rightarrow 2[CaS] + (O_2)$	43,780		−1.70	5	300 to 1,000		combination of first 2 equations for Ca compounds. In fair agreement with equation resulting from USBS circ. 500 (15) data
$[CaO] + (CO_2) \rightarrow [CaCO_3]$	−42,400		37.7	1	298 to 1,150	(9) Table E	
$[CaS] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [CaCO_3] + \frac{1}{2}(S_2)$	−68,900		39.7	4	300 to 1,000	(9) Table A	
$[CaSO_4] + (CO_2) \rightarrow [CaCO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2)$	163,500		−46.3	5	300 to 1,000	(9) Table A	
$[CaCO_3] + (F_2) \rightarrow [CaF_2] + (CO_2) + \frac{1}{2}(O_2)$	−95,900		−21.3	5	300 to 1,000	(9) Table A	
$[Ca] + (F_2) \rightarrow [CaF_2]$	−290,300		42.0	5	300 to 1,000	(9) Table A	
$[CaCO_3] + [SiO_2] \rightarrow [CaSiO_3] + (CO_2)$	17,130		−32.8	ca. 3	700 to 1,000		calculated from Ellis and Fyfe (3)
	21,190		−37.6	3	300 to 1,000	(9) Table E	
$[CaS] + [SiO_2] + \frac{1}{2}(O_2) \rightarrow [CaSiO_3] + \frac{1}{2}(S_2)$	−43,075		0.9	4	300 to 1,000	(9) Table E	
$[CaSiO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [CaSO_4] + [SiO_2]$	−184,700		84.6	6	300 to 1,000	(9) Table A	
(17) *Magnesium*							
$2[Mg] + (O_2) \rightarrow 2[MgO]$	−288,700	−5.90	67.90	3	298 to 923	(9) Table E	
$2[Mg] + (O_2) \rightarrow 2[MgO]$	−290,700	−0.48	53.90	3	923 to 1,380	(9) Table E	
$2[Mg] + (S_2) \rightarrow 2[MgS]$	−199,300		45.6	10	298 to 923	(9) Table E	
$2[Mg] + (S_2) \rightarrow 2[MgS]$	−203,600		51.3	10	923 to 1,380	(9) Table E	
$2[MgS] + (O_2) \rightarrow 2[MgO] + (S_2)$	−89,400	−5.90	22.3	13	298 to 923	(9) Table E	
$[MgO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [MgSO_4]$	−177,300		85.3	6	300 to 1,000	(9) Table A	
$[MgS] + 2(O_2) \rightarrow [MgSO_4]$	−222,500		86.3	8	300 to 1,000	(9) Table A	
$[MgO] + (CO_2) \rightarrow [MgCO_3]$	−28,100		40.6	3	298 to 1,000	(9) Table E	
$[MgS] + \frac{1}{2}(O_2) + (CO_2) \rightarrow [MgCO_3] + \frac{1}{2}(S_2)$	−72,800	−2.95	51.7	8	300 to 1,000	(9) Table E	

APPENDIX—*Continued*

Reaction	A	B	C	± Kcal	Temp. range (° K)	Source	Comments
$[MgCO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [MgSO_4] + (CO_2)$	−149,200		44.7	9	300 to 1,000	(9) Table E and Table A	
$2[MgS] + 2[SiO_2] + (O_2) \rightarrow 2[MgSiO_3] + (S_2)$	−107,200	−5.90	24.5	15	300 to 1,000	(9) Table E	
$[MgSiO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [MgSO_4] + [SiO_2]$	−168,400		84.2	7	300 to 1,000	(9) Table E and Table A	
(18) *Strontium*							
$2[Sr] + (O_2) \rightarrow 2[SrO]$	−282,000		48.0	5	300 to 1,000	(9) Table A	
$2[Sr] + (S_2) \rightarrow 2[SrS]$	−247,300		46.4	19	300 to 1,000	(9) Table A	
$2[SrS] + (O_2) \rightarrow 2[SrO] + (S_2)$	−34,700		1.6	23	300 to 1,000	(9) Table A	
$[SrS] + 2(O_2) \rightarrow [SrSO_4]$	−237,200		86.3	15	300 to 1,000	(9) Table A	
$[SrO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [SrSO_4]$	−219,800		85.5	9	300 to 1,000	(9) Table A	
$[SrO] + (CO_2) \rightarrow [SrCO_3]$	−56,100		40.9	4	300 to 1,000	(9) Table A	
$[SrS] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [SrCO_3] + \frac{1}{2}(S_2)$	−73,500		41.7	11	300 to 1,000	(9) Table A	
$[SrCO_3] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [SrSO_4] + (CO_2)$	−163,700		44.6	13	300 to 1,000	(9) Table A	
(19) *Barium*							
$2[Ba] + (O_2) \rightarrow 2[BaO]$	−265,600		46.4	8	298 to 983	(9) Table E	
$2[Ba] + (O_2) \rightarrow 2[BaO]$	−272,000		53.2	10	983 to 1,600	(9) Table E	
$2[Ba] + (S_2) \rightarrow 2[BaS]$	−243,100		42.8	15	300 to 1,000	(9) Table A	
$2[BaO] + (S_2) \rightarrow 2[BaS] + (O_2)$	22,500		−3.6	22	300 to 1,000	(9) Table A and Table E	
$[BaS] + 2(O_2) \rightarrow [BaSO_4]$	−244,200		88.4	13	300 to 1,000	(9) Table A	
$[BaO] + \frac{1}{2}(S_2) + \frac{3}{2}(O_2) \rightarrow [BaSO_4]$	−232,700		85.9	8	300 to 1,000	(9) Table A	
$[BaO] + (CO_2) \rightarrow [BaCO_3]$	−63,000		41.1	10	300 to 1,000	(9) Table A	
$[BaS] + (CO_2) + \frac{1}{2}(O_2) \rightarrow [BaCO_3] + \frac{1}{2}(S_2)$	−74,500		43.6	15	300 to 1,000	(9) Table A	
$[BaSO_4] + (CO_2) \rightarrow [BaCO_3] + \frac{1}{2}(S_2) + \frac{1}{2}(O_2)$	169,700		−44.8	14	300 to 1,000	(9) Table A	
(20) *Carbon*							
$[C] + (O_2) \rightarrow (CO_2)$	−94,200		−0.2	1	298 to 2,000	(9) Table E	

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SULFIDE PARAGENESIS IN THE EASTERN METALS DEPOSIT, MONTMAGNY COUNTY, QUEBEC

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ABSTRACT

The Eastern Metals deposit, Montmagny county, Quebec, is characterized by two sub-parallel zones of mineralization approximately 400 feet apart on the surface. The nickel minerals millerite, gersdorffite, and violarite have been identified in the North zone and chalcopyrite is the ore mineral of the South zone. Sphalerite is present in each zone. The ores are localized in zones of silicification and carbonatization along the contact between a serpentinized peridotite and slate fingers penetrating into the southwest end of the peridotite. The mineralization is postulated to have come about by the dissolving of separate pods of copper and nickel sulphides that originated during the crystallization of the peridotite. The agent responsible for the solution and deposition of the sulfides was oxidizing solutions that accompanied the intrusion of granodiorite dikes. The minerals were deposited in the alkaline environment of the silica-carbonate zone. The sphalerite was derived from the surrounding sediments by solution by the same solutions that carried the copper and nickel.

INTRODUCTION

DURING the winter of 1955, the writer had the opportunity of studying a suite of specimens from the Eastern Metals mine in the Eastern Townships of the Province of Quebec. The deposit is characterized by parallel zones of copper and nickel mineralization separated by serpentinized peridotite.

The presence of nickel was first reported in 1949 and in 1951 the mining rights were purchased by Ascot Metals Corporation. The property was being developed by the Eastern Metals Corporation Limited, a subsidiary of Ascot Metals, at the time of the writer's visit. It has since been acquired by Mogul Mining Corporation. The deposit attracted attention due to the suite of unusual nickel minerals. During the summer of 1952, Blais mapped the property for the Quebec Department of Mines. The results of his investigation appear in an unpublished report (2) and in the final report of the St. Magloire area by Béland (1).

The prime purpose of this paper is to describe the unusual relationships amongst the nickel minerals gersdorffite, millerite, and violarite; the differing mineralization in the two zones; and the possible origin of the deposit.

Location.—The Eastern Metals mine is situated in Rolette township, Montmagny county, in the Province of Quebec (Fig. 1). The mineral rights comprise lots 16–24, range 4; lots 12–29, range 5; lots 12–30, range 6; and lots 14–31, range 7, in Rolette township. Geographically, the property is located approximately 55 miles east-southeast of Quebec City and, from there can be reached by good, gravel-surfaced roads, or by railroad from Lac Frontière or Daaquam.

GENERAL GEOLOGY

The deposit is situated in the northeastern extremity of the Appalachian geologic province. The sedimentary and volcanic rocks in this area, ranging in age from Cambrian (?) to Devonian, have been folded along east-northeast axes so that they now have steep to vertical and even overturned dips in places. During the processes of folding the rocks were transformed into slates and schists. Pretectonic peridotites and pyroxenites occur in a linear belt stretching from the Shickshock mountains of the Gaspé peninsula southwestward to the Green mountains of Vermont (Fig. 1). The latest intrusive rocks of the region are post-Devonian granite batholiths. The closest one to the deposit is some 72 miles to the southwest.

The ore is located within zones of silicification and carbonatization at the contact between Ordovician Beauceville slates and a peridotite mass that has been intruded into the slates. The peridotite is in contact to the north with the Cambrian (?) Caldwell volcanics (Fig. 2). The major axis of the peridotite body is one and one-quarter miles long in a northeasterly direction and is three-eighths of a mile across at its widest part. At the southwestern extremity there is a large embayment of slates penetrating about one-half mile into the main body of the peridotite. In detail, the embayment can be divided into four separate digitations. Blais (2) reports that the southeast side of the peridotite dips steeply to the southeast, the northwest side dips 45° NW, and the west end plunges 45° SW. In the immediate vicinity of the ore deposit, the peridotite is dark green to bluish-black and has been extensively

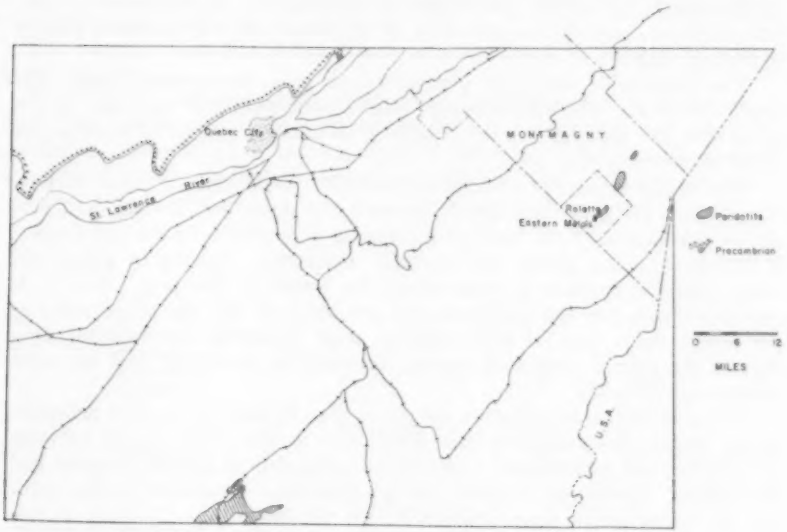

FIG. 1.

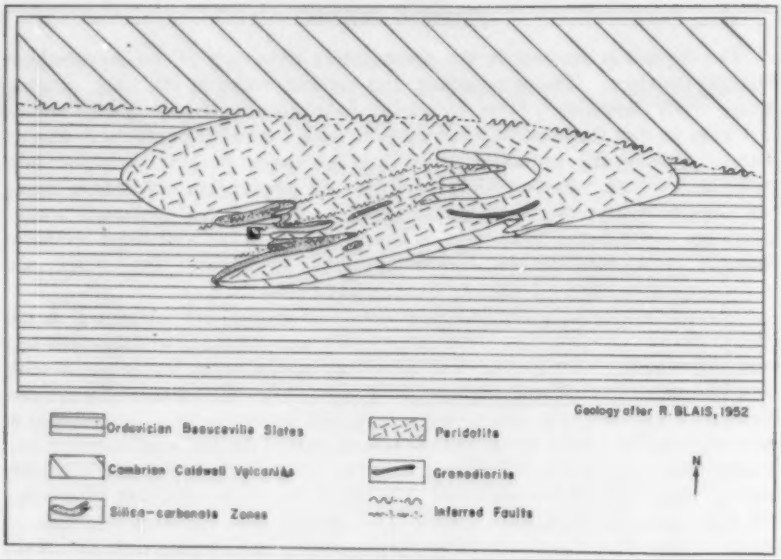

FIG. 2. Scale, 1 inch = 0.16 mile.

serpentinized, brecciated, and veined by carbonates. Several vertical granodiorite dikes, varying in width from 20 to 50 feet, cut the peridotite parallel to its long axis.

The Beauceville slates are generally dark gray, fine-grained, fissile, and locally phyllitic. The slaty cleavage strikes northeast, dips vertically, and is parallel to the bedding. A few, black, graphitic zones were outlined in the South zone on the first level.

The ore is intimately associated with rocks of the silicified and carbonatized zones lying at the contacts between the slates and the peridotites at the southwest end of the peridotite. The rock produced by the silicification is dark gray, dense, cherty, and partially brecciated. Veining by glassy and milky quartz is common in areas where the fracturing has been intense. It seems probable that the silicification of the bed-rock and the introduction of the quartz veins were of two different ages. Spatially, the silicified zone follows the jagged southwest contact between the peridotite and the slate embayment (Fig. 2).

The zones of carbonatization consist of fine- to medium-grained dolomite, locally vuggy, and veined by later calcite and quartz. The contact between the silicified and carbonatized zones is difficult to delimit as it is irregular and gradational. Generally, however, the silicified zone is adjacent to the slates and the carbonatized zone adjacent to the peridotite. Local zones of talc schist are frequently encountered in the silica-carbonate zone.

The interpretation of detailed structure is extremely difficult because of the lack of fossils, marker horizons, and the tight folding and alteration of the sediments and volcanics. Béland (1) has postulated a major fault immediately north of the peridotite at the contact with the Caldwell volcanics. Although no other faults have been recognized on the property, it is possible that the zones of silicification and carbonatization occupy zones of dislocation (Fig. 2). The presence of such faults would explain the highly irregular slate-peridotite contact in the vicinity of the ore and would also afford channelways for the mineralizing solutions. It is interesting to note in this connection that Hobbs and Pecora (7) mapped similar silica-carbonate zones localized along faults in a serpentinite in the State of Washington.

MINERALIZATION

The mineralization at Eastern Metals is principally confined to two subparallel zones; a northern nickel zone (North zone) and a southern copper zone (South zone). One of the most interesting features of the deposit is the nearly total absence of copper in the nickel zone and of nickel in the copper zone. This problem will be discussed in the section of this paper dealing with the origin of the deposit.

North Zone

The North zone is a tabular body confined practically wholly to a silica-carbonate zone lying immediately south of the northernmost slate embayment (Fig. 2). It strikes N 25° E and dips vertically. Blais (2) reports that it plunges to the southwest at an angle of 45°.

The minerals identified in the North zone are listed in Table 1 in paragenetic sequence.

In addition, pyrrhotite occurs as films on slip surfaces within the serpentine. The relative age of the pyrrhotite in the paragenetic sequence was not established. Marcasite has been reported by Béland (1) and the uncommon secondary minerals, hisingerite, allophane, lutecite, and cyanotrichite have

TABLE 1

Mineral	Stage
Violarite	4
Gersdorffite	
Millerite, sphalerite	B
Pyrite 2	3
Quartz	
Calcite	A
Brecciation	
Pyrite 1	
Silicification-carbonatization	2
Faulting	
Serpentine	
Chromite	1

been identified by Faessler (6). Two X-ray fluoresence analyses were made of material from the North zone. They indicated an absence of cobalt.

Since this paper is primarily concerned with the paragenetic relationships among the sulphides, only these will be discussed.

Pyrite.—Two ages of pyrite have been recognized. The first of these makes up approximately 90 per cent of the total amount. It is generally massive, showing no outward crystalline form. Under the microscope the individual masses are composed of a mosaic of weakly anisotropic grains, an apparent result of brecciation. Veins and stringers of later quartz and calcite criss-cross the pyrite and in places fill the spaces between the individual fragments. In some places angular chips of pyrite completely enclosed by calcite, can be traced back into corresponding reentrants in the main mass of pyrite (Fig. 3a). The second age of pyrite is represented by veinlets of a fresher, non-brecciated type cutting the former brecciated pyrite and the rocks of the silica-carbonate zone. It also occurs in the quartz veins. This pyrite marks the advent of the deposition of the nickel-bearing minerals.

Millerite.—Millerite was observed on both the first and third levels of the mine. On the first level it is associated with pyrite in narrow quartz stringers and on the third level it appears in the form of closely-spaced crystals up to one inch in diameter occurring in seams of clayey material. In the latter place the crystals are brass-yellow, crumbly, and possess two good cleavage planes parallel to the $(10\bar{1}1)$ and $(01\bar{1}2)$ faces. It resembles pyrite in hand specimen but can be distinguished by its lesser hardness. A polished section of one of these crystals was studied under the mineralographic microscope. The millerite appeared massive and there was no tendency to the radiating or tufted structure that generally characterizes this mineral, according to Dana (4). It is apparently similar to the millerite found at Alistos, Mexico, by Krieger and Hagner (8). Some millerite was also observed along slip planes in the serpentine.

An X-ray diffraction analysis of the same crystal from which the polished section was made, matched very well the pattern obtained from a laboratory sample, location unknown. The d-spacings also checked with the data for millerite on the A. S. T. M. cards.

Gersdorffite.—Gersdorffite was not identified in hand specimens, but under the microscope it was seen to occur as tiny blebs and aggregates scattered through the silica-carbonate rock. It was found bordering millerite in several places (Fig. 3b).

Violarite.—Violarite appears as an alteration product of both millerite and gersdorffite and is therefore found intimately associated with them (Fig. 4a). It was also observed as selvages and seams along the schistosity planes of a talc schist on the third level. The mineral alters readily on exposure to the atmosphere and is sometimes difficult to identify in hand specimen.

Sphalerite.—The sphalerite occurs as narrow, irregular stringers associated with the millerite. None was seen in hand specimen, but it was readily identified in polished section.

Paragenesis.—The paragenetic sequence of mineralization in the North zone can be divided into three, and possibly four stages (Table 1). The

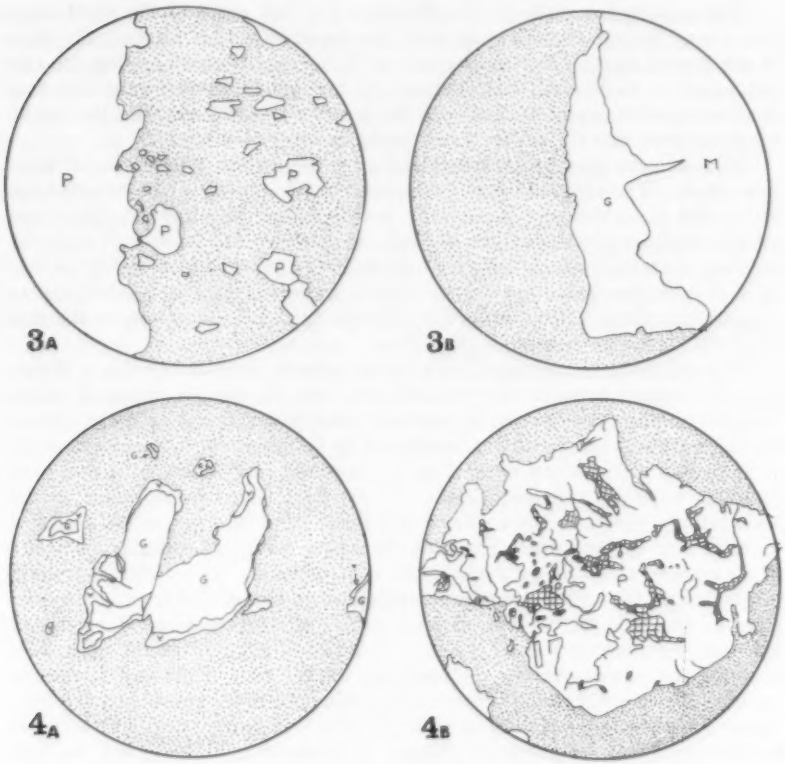

FIG. 3a. Frittering of pyrite at contact with carbonate gangue. Note the angularity of the pyrite fragments. P-pyrite; stippled-gangue. × 100.

FIG. 3b. Gersdorffite replacing millerite. G-gersdorffite; M-millerite; stippled-gangue. × 100.

FIG. 4a. Violarite replacing gersdorffite. Note the various stages in the process of replacement as represented by the smaller grains. G—gersdorffite; V—violarite; stippled-gangue. × 430.

FIG. 4b. Early stage of the replacement of pyrite by chalcopyrite. P—pyrite; cross-hatched—chalcopyrite; stippled—gangue. × 100.

first stage includes the introduction of the peridotite, with accessory chromite, and the serpentinization of the peridotite. The close of this stage was marked by faulting which was accompanied by, or shortly followed by, silicification and carbonatization of the slates and serpentine. This was succeeded by a major inundation of pyrite, which replaced, to a certain extent, the silica-carbonate rocks. The close of this stage was marked by renewed movement along the faults and brecciation of the silica-carbonate rock, serpentine, chromite, and pyrite.

The veining by calcite is considered as the first event of the third stage but it may be contemporaneous with the brecciation that marked the close of the second stage. No direct evidence of the quartz veins cutting the calcite veins, or vice-versa, was observed by the writer, however the fact that the later sulfides are associated with the quartz veins and not with the calcite veins suggests that the calcite was introduced before the quartz.

The younger pyrite was introduced after the quartz and fills small fractures in it. The millerite found in the quartz veins in the first level replaces the pyrite along cleavage planes and peripherally. Although no direct age relationships were observed for the millerite of the third level, it is assumed as being contemporaneous with that of the first level. The possibility of two ages of millerite should not be overlooked, however, there is no evidence to support this idea. The gersdorffite replaces the millerite wherever the two minerals were seen in contact (Fig. 3b).

The sphalerite is associated with the millerite in the quartz veins. Wherever the contact between the two minerals was observed it appeared either straight, or was characterized by *mutual boundary* texture. By these criteria the millerite and sphalerite are considered to be essentially contemporaneous.

Violarite was the last mineral to be deposited. It occurs in and around both the millerite and gersdorffite. Under high magnification tiny cracks and cleavage planes in the millerite and gersdorffite are seen to be bordered on each side by violarite. The violarite has a scalloped edge, i.e., a series of connecting arcs convex towards the host mineral. The violarite borders can be traced through the fractures and cleavage planes and around the outsides of the millerite and gersdorffite grains separating them into islands. Various stages of this alteration can be observed in different grains (Fig. 4a). In some places violarite has replaced over 90 per cent of the gersdorffite or millerite and it is therefore believed that grains of pure violarite actually represent complete replacements of either millerite or gersdorffite. Violarite is usually considered an alteration product of pentlandite. This is not the case at Eastern Metals. The scalloped edges of the violarite in the intermediate stages of alteration are suggestive of a rather low-temperature phenomenon and it is possible that the violarite is a supergene mineral, and could be considered a fourth stage in the mineralization.

South Zone

The South zone is located in a silica-carbonate zone bordering the southern side of the southernmost slate finger of the embayment (Fig. 2). The northeast end of the zone is 400 feet southeast and 150 feet southwest of the southwest end of the North zone. The zone strikes N 25° E and dips 45° northwest. It plunges 45° to the southwest. The minerals identified in the South zone are listed in paragenetic sequence in Table 2.

The alteration minerals reported by Faessler and listed in the description of the North zone also occur in the South zone. Béland (1) also records the presence of chalcocite.

X-ray fluoresence of material containing chalcopyrite, sphalerite, and galena indicated, as well as the presence of copper, zinc, and lead, a mod-

erately strong K-alpha line for cadmium and weak L-beta$_1$ and L-beta$_2$ lines for platinum. The cadmium is probably contained in the sphalerite. No platinum-bearing minerals were noted in the polished sections examined, but it is not unlikely that some may be associated with the peridotite. No gold or silver were found in the polished sections and none was indicated in the X-ray analyses. Both are reported in the assay records of the South zone. Blais (2) records the presence of a silvery-gray silver mineral, but was unable to identify it positively. The absence of this mineral in the writer's sections probably indicates that the silver mineralization occurs in pockets.

Pyrite.—Two ages of pyrite were also identified from the South zone. The first of these is confined to the black, graphitic slates and appears as brecciated, discrete cubes giving an exploded texture to the pyrite. It is probable that this pyrite is authigenetic. The second age of pyrite is similar in all respects to that representing the first age in the North zone. No evidence of the pyrite corresponding to the second age in the North zone was observed in the South zone.

TABLE 2

Mineral	Stage	
Bornite		
Chalcopyrite, sphalerite, galena	B	
Arsenopyrite		3
Quartz	A	
Calcite		
Brecciation		
Pyrite 2		
Silicification-carbonatization		2
Faulting		
Serpentine		
Chromite		1
Pyrite 1		

Arsenopyrite.—One small grain of arsenopyrite was detected in a polished section. It is being replaced by chalcopyrite and is surrounded by sphalerite. Blais (2) reports that it is quite abundant in one of his polished sections.

Chalcopyrite.—The chalcopyrite is the main copper-bearing mineral of the South zone. It occurs in massive form replacing the pyrite and silica-carbonate rock, or as chalcopyrite-rich seams and veins cutting and replacing the host rocks. Under the microscope it was seen to occur in a number of different ways. It is present in the graphitic slates as tiny en-echelon lenses; elongated, irregular replacement masses; and as frittered grains with projections along the planes of slaty cleavage. The bulk of the remainder of the chalcopyrite is intimately associated with the pyrite and sphalerite and these relations will be discussed in the paragraphs dealing with the paragenesis of the South zone.

Sphalerite.—The sphalerite occurs as isolated, microscopic patches intimately associated with the chalcopyrite. In some grains a lattice-work of chalcopyrite has developed along the dodecahedral cleavage planes of the sphalerite (Fig. 5b).

FIG. 5a. More advanced stage in the replacement of pyrite by chalcopyrite. C—chalcopyrite; P—pyrite; stippled—gangue (marked Q when quartz). × 100.

FIG. 5b. Chalcopyrite-sphalerite relationships. Note the chalcopyrite working into the sphalerite cleavage planes in the center; the incipient pseudo-eutectic texture in the bottom, right-hand side; and the sphalerite apparently replacing the chalcopyrite in the upper-left. S—sphalerite; P—pyrite; cross-hatched—chalcopyrite; Q—quartz. × 430.

Galena.—Several minute grains of a light bluish-gray (color in polished section) mineral were tentatively identified as galena. They occur as isolated blebs in the chalcopyrite and sphalerite.

Bornite.—A few small specks of bornite were observed under the binocular microscope in one specimen. None was observed in polished section. Béland (1) suggests that it is an alteration product of chalcopyrite.

Paragenesis.—The paragenetic sequence of mineralization in the South zone can be divided into three stages (Table 2). The sequence up to and including the introduction of the quartz veins is the same as that in the North zone with the exception of the authigenetic pyrite, which is absent in the North zone.

A certain amount of the vein quartz has chalcopyrite associated with it and, although the bulk of the chalcopyrite appears as a replacement of the silica-carbonate rock and pyrite, it is believed that it was introduced shortly after the quartz and probably along the same channelways.

The one grain of arsenopyrite observed was enclosed in the silica-carbonate rock and is replaced along its cleavage and fracture planes by chalcopyrite and is rimmed by sphalerite. The arsenopyrite is therefore earlier than the chalcopyrite. In addition, it is post-brecciation as the grain is not shattered, as was noted with the pyrite and chromite.

The sphalerite, chalcopyrite, and galena form a distinct phase in the paragenesis. The sphalerite and chalcopyrite ages overlap to a certain extent. Chalcopyrite was seen replacing pyrite, arsenopyrite, and sphalerite.

All stages of replacement of the pyrite by the chalcopyrite were observed.

The first stage shows tiny step-veinlets of chalcopyrite following the cleavage planes of the pyrite. These veinlets start at the borders of the pyrite grains and wedge out towards the center (Fig. 4b). The next stage is the joining of these veinlets leaving isolated, generally straight-edged pyrite remnants. The chalcopyrite then seems to proceed into the cleavage planes of these isolated remnants and eventually an excellent pseudoeutectic texture is produced. At this stage the periphery of the pyrite has been completely replaced and the small lattice-veinlets can be traced into the massive chalcopyrite of the border phase. Next, an explosion texture is produced. The lattice-veinlets replace the pyrite inwards, resulting in scattered pyrite fragments "floating" in a sea of chalcopyrite. The ultimate stage is the complete replacement of the pyrite. A more advanced stage of replacement is indicated in Figure 5a.

Paragenetic relationships between the sphalerite and the chalcopyrite are contradictory. A preponderance of evidence indicates that the chalcopyrite is later than the sphalerite, but, on the other hand, there is certain evidence to support the converse. Excellent pseudoeutectic textures were observed between the chalcopyrite and the sphalerite, with the sphalerite acting as host. It resembles the texture described above between the pyrite and the chalcopyrite, except that in this case, the replacement has taken place along the dodecahedral cleavage planes of the sphalerite. The outer borders of the sphalerite have been replaced by the chalcopyrite and the replacement veinlets within the sphalerite can be traced into this border phase. Where the replacement veinlets intersect, there is a widening at the junction, such as would be the case in a replacement texture (Fig. 5b). There appears to be no question that the chalcopyrite is later than the sphalerite. On the other hand, sections were examined that show the peripheral replacement of chalcopyrite by sphalerite. It is therefore concluded that the two minerals are contemporaneous.

The galena occurs as isolated blebs within the chalcopyrite and the sphalerite and also as little veinlets cutting the silica-carbonate rock. It is difficult to determine the age relationships between the galena and the other sulfides from the polished sections examined. If the general close association between galena and sphalerite is also prevalent at Eastern Metals, then the two minerals may be considered contemporaneous, or nearly so, and the galena would therefore be of approximately the same age as the chalcopyrite.

Bornite was not observed in polished sections examined but in a hand specimen studied under the binocular microscope, it was observed replacing chalcopyrite. If the bornite is supergene, it may be related in time to the production of violarite in the North zone.

COMPARISON WITH OTHER DEPOSITS

A review of the literature reveals that the Eastern Metals deposit is uncommon. The presence of violarite replacing millerite and gersdorffite has, as far as I have been able to ascertain, not been recorded elsewhere.

At Alistos, Sinaloa, Mexico, Krieger and Hagner (8) report pentlandite and gersdorffite cutting and replacing millerite. As mentioned previously,

the millerite in this district closely resembles that from Eastern Metals. According to Krieger and Hagner (8): "It (millerite) is judged to be hypogene because of its character and the fact that it is cut by veinlets of both pentlandite and gersdorffite." The pentlandite shows extensive replacement by violarite and, in all places observed, this alteration stops abruptly at the contacts between pentlandite and gersdorffite and pentlandite and millerite. In other words, the violaritization is confined wholly to the pentlandite.

The alteration of pentlandite to violarite is also reported from Dracut, Massachusetts, by Dennen (5), Levack mine in the Sudbury district, by Wandke and Hoffman (12), and from the Cuniptau mine, Ontario, by Sandefur (10). Buddington (3) writes that pentlandite is being replaced by mineral X in some nickel prospects in Alaska and at the Key West mine, Nevada, Lindgren and Davy (9) mention the replacement of pentlandite by polydymite. Short and Shannon (11) believe that the mineral X of Buddington and the polydymite of Lindgren and Davy are actually violarite, and identify it as being the same as the violarite of the Sudbury district. At the Vermillion mine, violarite and pentlandite are not found together and Short and Shannon (11) believe that violarite is either a complete replacement of pentlandite or that unknown conditions favored the development of violarite rather than pentlandite. They also report the presence of violarite being replaced by millerite.

The replacement of pyrrhotite by violarite was reported from the Cuniptau mine by Sandefur (10), and from Alaska by Buddington (3). At Dracut, Massachusetts, Dennen (5) records both pyrrhotite and pentlandite in the ore, but states that violarite replaces only the pentlandite.

DISCUSSION

From the above survey, it is apparent that the conditions at Eastern Metals are unique. The writer believes that the millerite is hypogene, (a) because of its unusual massive character, and (b) because of the fact that it is cut by gersdorffite, which is generally considered to be a hypogene mineral.

Violarite was found replacing both millerite and gersdorffite. There is, therefore, no reason to assume that violarite is necessarily an alteration product of only pentlandite or, in a few places, nickeliferous pyrrhotite. It is apparent, however, that these types of replacement would be more common, in that all three minerals involved (violarite, pentlandite, nickeliferous pyrrhotite) are essentially sulphides of iron and nickel. The replacement of gersdorffite by violarite involves the liberation of arsenic and, perhaps, the introduction of iron, although some varieties of gersdorffite do contain iron, perhaps in sufficient quantity to account for all of that found in the violarite. Unfortunately the gersdorffite at Eastern Metals was not analyzed for its iron content. The replacement of millerite by violarite involves the introduction of iron. The relations outlined in this paragraph further complicate the already complex problem of nickel-bearing sulphides and it is hoped that this information may aid some person involved in the geochemical study of these minerals.

A comparison of the parageneses of the North and South zones presents

one of the most interesting features connected with the Eastern Metals deposit. The writer feels that the sequence of events up to, and including the introduction of the quartz veins was simultaneously developed in the two zones. The fact that a brecciated, pyritized silica-carbonate rock is present in each zone lends support to this conclusion. It is difficult to assume that two, independent, similar processes, acting at different times produced exactly the same type of mineralization in the two zones. Calcite and quartz veins are found in each zone preceding the main period of ore mineralization. It is assumed here that they were also developed simultaneously in the two zones.

Following the introduction of the quartz, there is a clean-cut and puzzling divergence of mineralization in the two zones. Copper mineralization with slight traces of nickel is found in the South zone and nickel mineralization with traces of copper developed in the North zone. The "traces" of nickel and copper mentioned above are found in assay reports, but the writer saw no minerals in the specimens examined that could possibly account for these "traces."

The divergence of mineralization renders it difficult to correlate the post-quartz vein mineralization in the North and South zones. There are possibly several ways to explain the divergence:

(1) It is possible that the ore mineralization was developed simultaneously in the two zones and that the difference in character is a reflection of local chemical changes in the solutions brought about by differences in the wall-rock in the North and South zones. A study of these wall-rocks reveals, however, that they are practically identical in the two zones. Both are characterized by the development of zones of silicification and carbonatization at slate-peridotite contacts. It does not seem possible, therefore, that this is a practical hypothesis.

(2) A second possibility is that either one of the zones may have developed first. This may have been followed by a sealing of this zone, a change in content of the mineralizing solutions, and a diversion of the changed solutions into the second zone, leading to a different suite of minerals. If this is the case, the mineralization of the two zones must have been separated by a period of time long enough to allow for the complete change of the solutions from nickel-bearing to copper-bearing or vice-versa, depending on which of the zones was mineralized first. This hypothesis, although possible, appears to involve a series of extremely fortuitous circumstances.

(3) A third possibility is that the two zones may have two different sources, with separate channelways. This would imply that the mineralization could take place independently in the two zones and at approximately the same time. At the surface the North and South zones are separated by 400 feet of serpentinized peridotite and slates. The fact that the North zone is vertical and that the South zone dips at an angle of 45° towards it, implies that the two zones intersect at depth. As will be pointed out below, however, the writer feels that the two zones remain separated at depth.

The presence of sphalerite in the two zones suggests that it was added at the same time. There is no evidence leading to the conclusion that there are two ages of sphalerite. If, then, the sphalerite in the North and South

zones is of the same age, it follows that the millerite in the North zone, and the chalcopyrite and galena in the South zone were being deposited at the same time, as each one of these minerals is considered as contemporaneous with sphalerite. This could only mean that the copper and nickel were derived from two different sources and were deposited in two separate zones with no intermingling of solutions. It further indicates that the sphalerite was present in both source areas, or was added to both solutions as they rose along their respective channelways. Copper and nickel are commonly associated with ultrabasic rocks and I feel that this is the case at Eastern Metals. The granodiorite dikes are later than the peridotite, but, due to their small size, it is difficult to postulate them as a source of the copper and nickel. There are no indications of larger intrusions in the immediate area that could have served as source. Sphalerite, on the other hand, is not a common accompaniment of peridotite and was probably derived from another source.

In view of the above interpretations, I offer the following hypothesis for the origin of the Eastern Metals deposit.

During the crystallization of the peridotite and the accumulation of olivine and pyroxene by gravitational settling, it is possible that pods of copper and nickel sulphides accumulated at the same time either by early crystallization or by crystallization from an immiscible sulphide liquid fraction, and were enclosed in the peridotite. The dissimilarity between the ore of the North zone and that of the South zone is the result of an original accumulation of copper-sulphides in one pod and nickel-sulphides in another. It is assumed that the original nickel mineral was pentlandite and/or nickeliferous pyrrhotite, and the original copper mineral, chalcopyrite. The original separation into the two pods was probably a function of the specific gravity of the sulphide involved. The intrusion of the granodiorite dikes was probably contemporaneous with the movement that brecciated the pyritized silica-carbonate rock. The solutions that accompanied the granodiorite leached the pods of sulphides and redeposited the material in the reducing environment of the silica-carbonate zone. The minerals deposited were chalcopyrite, millerite, and gersdorffite.

Sphalerite is not ordinarily associated with ultramafic rocks and it is difficult to call on the granodiorite dikes as a source of the zinc. The only alternative is that the zinc was once an original constituent of the sedimentary rocks in the region and was dissolved by the same solutions that redistributed the copper and nickel. This would account for the presence of sphalerite in the two zones. Unfortunately no analyses of the amount of zinc distributed in the sediments of this district are available.

An interesting sidelight on the mineralization in the two zones is the presence of gersdorffite (NiAsS) in the North zone and arsenopyrite (FeAsS) in the South zone. This indicates that the (AsS^{-2}) radicle has a preference for Ni^{+2} rather than for Fe^{+2}.

After the main period of mineralization in the two zones, violarite, bornite, and chalcocite were developed in their respective zones. The formation of these minerals may have been by a supergene process.

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CLASSIFICATION OF THE NONMETALLICS

ROBERT L. BATES

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ABSTRACT

A rational classification is a prerequisite for the systematic study of the geology of the nonmetallics. Neither the conventional treatment of the subject in standard references, nor a strictly genetic classification, is considered satisfactory for this purpose. Several criteria, primarily economic, are set forth, by which the nonmetallics are subdivided into two major groups, the industrial rocks and the industrial minerals. Further subdivision within each group is on the basis of origin. A proposed classification is presented and briefly discussed.

INTRODUCTION

THE earth materials essential to modern industrial civilization may be grouped in a general way as follows:

1. Metallic minerals.
2. Mineral fuels.
3. Ground water.
4. Nonmetallics.

Each of the first three is recognized as a legitimate subject for systematic geologic study. Each is treated in standard textbooks, and is the subject of courses regularly taught in geology departments. The scope of each field, and the individual materials to be considered within it, are relatively well agreed upon. The nonmetallics, on the other hand, have a sort of step-child status in the field of economic geology. No modern textbook is devoted exclusively to the geology of these materials, nor is a course in their geology taught in many departments.

Even the term "nonmetallics" itself is subject to different interpretations. Literally speaking, it includes items 2 through 4 in the above list—that is, everything that is not metallic. This usage was followed by Bayley (2) in 1930 (except for building stones, which he omitted from consideration).

Today, of course, the mineral fuels and underground water are granted their own sovereignty, and the term "nonmetallics" has come to mean "earth materials other than metals, coal, oil, gas, and water."

"Nonmetallics" is less than an ideal term on other grounds than imprecision. For one thing, it defines a subject by what it is not, rather than by what it is. Further, it can apply to manufactured products as well as to naturally occurring substances. For reasons to be indicated, the writer prefers the expression "industrial rocks and minerals," which is considerably more accurate and descriptive. "Nonmetallics," however, has one distinct advantage: it is a convenient, single word. It is used in this paper in the sense indicated in the above list.

There can be no doubt of the great economic importance of the nonmetallics. They are absolutely essential to the construction, chemical, ceramic, and other industries, and indeed the value of their annual production exceeds that of the metallic minerals. Thus it seems as logical to study and learn about the geology of the nonmetallics as about that of any of the other major groups. Yet the one prerequisite to systematic study—a rational classification—does not seem to exist. It is the purpose of this paper to explore this question, and to present a classification that appears valid and has been found useful in teaching.

CONVENTIONAL TREATMENT

There are in the field two recent standard reference works: Industrial Minerals and Rocks, second edition, of the A.I.M.E. (1); and Nonmetallic Minerals, by Ladoo and Myers (3). Supplementing these are two books which treat the entire field of mineral resources, the nonmetallics included: Mineral Facts and Problems, of the U. S. Bureau of Mines (5), and the invaluable Minerals Yearbook (6). All of these treat the subject matter in approximately the same order. From 35 to 90 nonmetallics are described, the number depending on the authors' preference in subdividing the group. As conventionally listed, the more important of these are given in Table 1.

TABLE 1

CONVENTIONAL LISTING OF THE MORE IMPORTANT NONMETALLICS

Abrasives	Magnesite
Asbestos	Mica
Barite	Nitrates
Borax	Perlite
Cement	Phosphate rock
Clay	Potash minerals
Crushed stone	Pumice and pumicite
Diamond	Quartz crystal
Diatomite	Refractories
Dimension stone	Salt
Feldspar	Sand and gravel
Fluorspar	Slate
Graphite	Sodium minerals
Gypsum	Sulfur
Lime	Talc
Lithium minerals	Vermiculite

Being alphabetically arranged, this listing is admirably suited for quick reference. Under each heading, data are found on properties, important deposits, mining and milling methods, utilization, prices, production figures, and general statistics. There is no question whatever of the usefulness of this arrangement for recording information of the type indicated.

But such a list is scarcely a basis for geologic study. One does not study the metallic minerals alphabetically. Besides, the list includes markedly different categories, as indicated in Table 2.

TABLE 2

CATEGORIES INCLUDED IN CONVENTIONAL LISTING

Minerals: asbestos, barite, etc.
Rocks: gypsum, phosphate rock, etc.
Groups of rocks: crushed stone, dimension stone.
Manufactured products: cement, lime.
Mixed groups: abrasives, refractories.

Minerals and rocks are of course logical subjects for geologic study; but it is irrational, or impossible, to study the geology of miscellaneous groups of rocks, manufactured products, or mixed natural and artificial substances. The lack of geologic relevance is apparent in such a group as the abrasives:

Minerals—diamond, corundum, garnet, etc.
Rocks—sandstone, pumice, diatomite, etc.
Manufactured products: silicon carbide, fused alumina, etc.

In Table 1, there is no entry for granite, basalt, marble, sandstone, or limestone. To find information on limestone as such, one must look under lime, cement, crushed stone, and dimension stone (and, in more inclusive lists, under chalk and whiting, lithographic stone, and so on). It is plain that the conventional treatment of the nonmetallics, which is based entirely on economics (how they are used), is unsuitable for a study of their geology (how they occur). Obviously a different approach is necessary.

GENETIC CLASSIFICATION

It is possible to adhere strictly to the geologic line, ignoring economic aspects altogether. Under this procedure, one might classify the nonmetallics under the three main heads of igneous, metamorphic, and sedimentary, with appropriate subdivisions of each. The metamorphic group, for example, might be arranged somewhat as follows:

Metamorphic.
  Dynamothermal: graphite, marble, slate.
  Hydrothermal: asbestos, talc.

At least two disadvantages with such a classification suggest themselves. One is that, in using it, the teacher or student must constantly move back and forth, from minerals to rocks and back again to minerals. The writer has

found from classroom experience that this is more distracting than might at first appear. The second, and more fundamental, objection is that the straight genetic classification is totally unrelated to economics, being as awkward to use in dealing with application as the conventional list is in dealing with occurrence. As Lasky (4) remarks, "The dividing line between geology and economics is vague;" and nowhere is it vaguer than in the nonmetallics. Thus we need to look in the middle ground, for a basis of classification that contains both economic and geologic elements.

BASIS FOR PROPOSED CLASSIFICATION

One of the anomalies of the conventional listing of the nonmetallics (Table 1) is that it includes such materials as crushed stone, gypsum, and sand and gravel, on a par with materials like industrial diamonds, sheet mica, and quartz crystal. The former trio differs sharply from the latter in several respects, for example bulk produced, unit value, and availability of deposits. It seems to the writer that there are several criteria, primarily economic, by which we may reasonably divide the nonmetallics into two major groups. These are listed in Table 3.

TABLE 3

CRITERIA FOR TWOFOLD SUBDIVISION OF THE NONMETALLICS

Aspect	Group 1	Group 2
Bulk	Large	Small
Unit value	Low	High
Place value	High	Low
Imports and exports	Few	Many
Distribution	Widespread	Restricted
Geology	Simple	Complex
Processing	Simple	Complex

Sand and gravel, for example, obviously belongs in Group 1. It is produced in enormous tonnages, and brings only a dollar or two per ton. The importance of place value is such that the maximum economic distance between deposit and market is less than a score of miles. Little if any enters into international trade. Deposits are numerous and widely distributed, and their geology is relatively simple. Processing of the product consists merely of washing and screening.

Most of these same aspects are possessed by crushed stone and gypsum. Industrial diamonds, high-grade mica, and quartz crystal, on the other hand, are at precisely the opposite extreme on nearly every count.

PROPOSED CLASSIFICATION

Application of the criteria of Table 3 to all the nonmetallics brings forth a clear conclusion: Group 1 of the table consists of rocks, and Group 2 consists of minerals. The primary subdivision, then, is into *industrial rocks* and *industrial minerals*, and it is made chiefly on the basis of mineral economics. As the ultimate aim is classification for geologic study, it seems

TABLE 4

PROPOSED CLASSIFICATION

Industrial rocks	Industrial minerals
Igneous	Pegmatite
Granite	Feldspar
Basalt	Mica
Pumice and pumicite	Lithium minerals
Perlite	Vein and replacement
Metamorphic	Quartz crystal
Slate	Fluorspar
Marble	Barite
Sedimentary	Magnesite
Sand and gravel	Metamorphic
Sandstone	Asbestos
Clay	Talc
Limestone and dolomite	Vermiculite
Phosphate rock	Graphite
Gypsum	Sedimentary and residual
Salt	Diamond
	Diatomite
	Potash minerals
	Sodium minerals
	Nitrates
	Borax
	Sulfur

logical to make the subdivisions within each group on a geologic (genetic) basis. The resulting classification, which the writer has used successfully in teaching, is set forth in Table 4.

DISCUSSION

In this combined economic-geologic classification, the rocks are separated naturally from the minerals. Genetically related materials—sedimentary rocks, pegmatite minerals, and so on—can be discussed together. Experience has shown that these are real advantages.

The objection may be made that, in applying the criteria of Table 3 to examples in an earlier paragraph, materials at opposite extremes were cited. How about the many nonmetallics that fall economically somewhere between? The writer has found relatively little difficulty on this count. Common salt is considered an industrial *rock* because it is produced in very large amounts from extensive deposits in at least half a dozen states, and possesses other aspects of Group 1 in Table 3. Potash salts are considered an industrial ***mineral*** because they are produced in much smaller tonnages, at higher prices, from only two deposits, and possess other aspects of Group 2. It will be found that each industrial rock and mineral fulfills most, if not all, of the criteria listed for the group in which it is placed. No more than this can be said for such analogous and widely accepted classifications as those of animals and plants.

The proposed classification commits the unpardonable sin of calling diatomite a mineral. (If nepheline syenite were included, it would also fall in the industrial-mineral column.) Of course diatomite is a rock by all commonly accepted petrologic standards. But, *by the criteria on which this classi-*

fication is based, it is an industrial mineral. To require a student to learn that diatomite is a rock in the course in petrology, but a mineral in the course in economic geology, is no more unreasonable than to teach him that coal is an organic rock by origin but a mineral fuel by use.

Other anomalies are present, but are masked by rock names. By the standards adopted, some of the special-purpose sands and high-grade clays may nearly as well be considered industrial minerals as industrial rocks. They are kept in the rock column so that their occurrence and origin may be discussed along with that of their less aristocratic relatives.

It may be pointed out, correctly, that this classification is so arranged that it will not quickly yield information about application and use. No artificial products, or mixed natural and artificial groups, are included. To find data on abrasives, one must look under a variety of headings. This, it will be noted, is the converse of the criticism levelled by the writer at the conventional list. It serves to point up a matter that needs emphasis: the classification proposed here is in no way intended to supplant, or substitute for, the conventional listing utilized in the standard references. It is not competitive but supplementary. It has resulted from looking at the nonmetallics from a different standpoint. The writer hopes that it will prove as useful a framework for geologic study as the conventional treatment has proved to be for statistical reference.

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AN OCCURRENCE OF RHENIUM ASSOCIATED WITH URANINITE IN COCONINO COUNTY, ARIZONA[1]

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ABSTRACT

Twenty-nine samples of sedimentary rocks of Triassic age from the Sun Valley uranium mine in northern Arizona were analyzed spectrographically; 11 of these samples contained 0.005 to 0.1 percent of the rare metallic element, rhenium.

The rhenium is associated with uranium and molybdenum (and probably with lead and zinc). It is probably in the form of the water soluble oxide (Re_2O_7) or perrhenic acid ($HReO_4$). The rhenium may have been contained originally in the mineral jordisite. This is indicated by the association of the rhenium oxide with the water-soluble molybdenum mineral, ilsemannite.

The Sun Valley mine is the only uranium deposit on the Colorado Plateau known to contain any rhenium.

INTRODUCTION

In the process of a routine semiquantitative spectrographic analysis for trace elements in a sample of uranium ore, an unusual amount (about 0.02 to 0.05 percent) of the rare metallic element, rhenium, was detected. Later, from 28 additional samples, 10 more were found to contain 0.005 to 0.1 percent rhenium.

The 29 samples used in this study came from the Sun Valley uranium mine in Coconino County, Ariz. The samples were collected in the summer

[1] Publication authorized by the Director, U. S. Geological Survey.

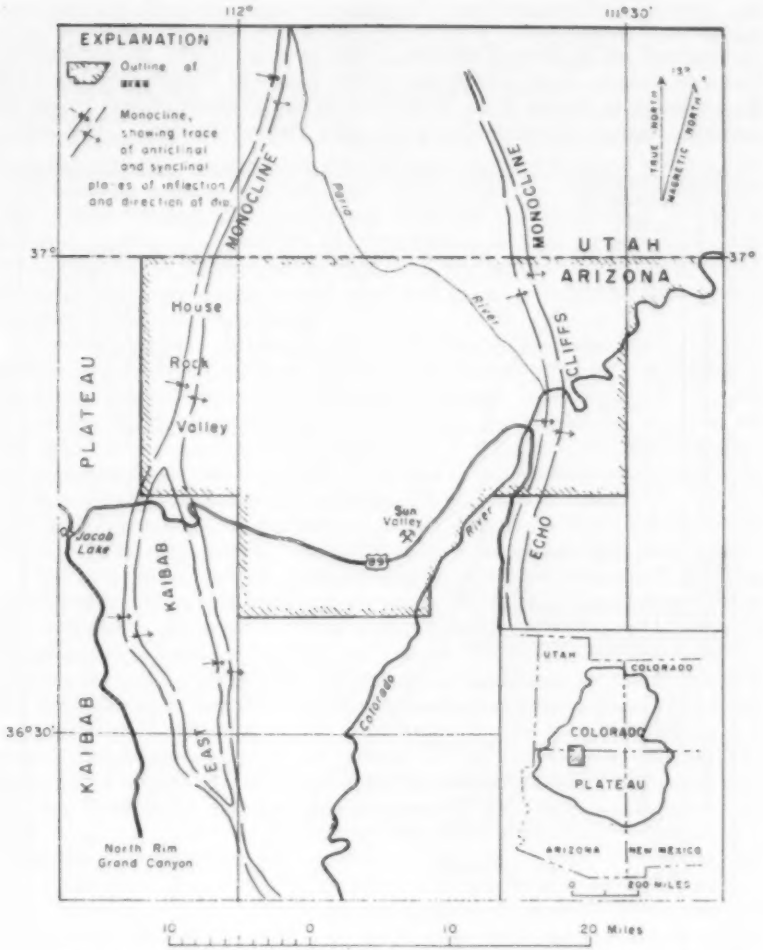

FIG. 1. Index map showing location of East Vermilion Cliffs area, Coconino County, Ariz.

of 1956, during geologic mapping and investigation of the East Vermilion Cliffs area (Fig. 1) by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

ACKNOWLEDGMENTS

The writers would like to thank the Uranium-Petroleum Company of Salt Lake City, Utah, for their permission to collect samples from the Sun Valley mine and to publish the data on them.

GEOLOGY

Regional.—The East Vermilion Cliffs area is located in north-central Coconino County, Ariz., and is part of the Colorado Plateau province (Fig. 1). Erosion in House Rock Valley and in the Colorado River Valley has exposed a section of sedimentary rocks more than a mile thick. This section

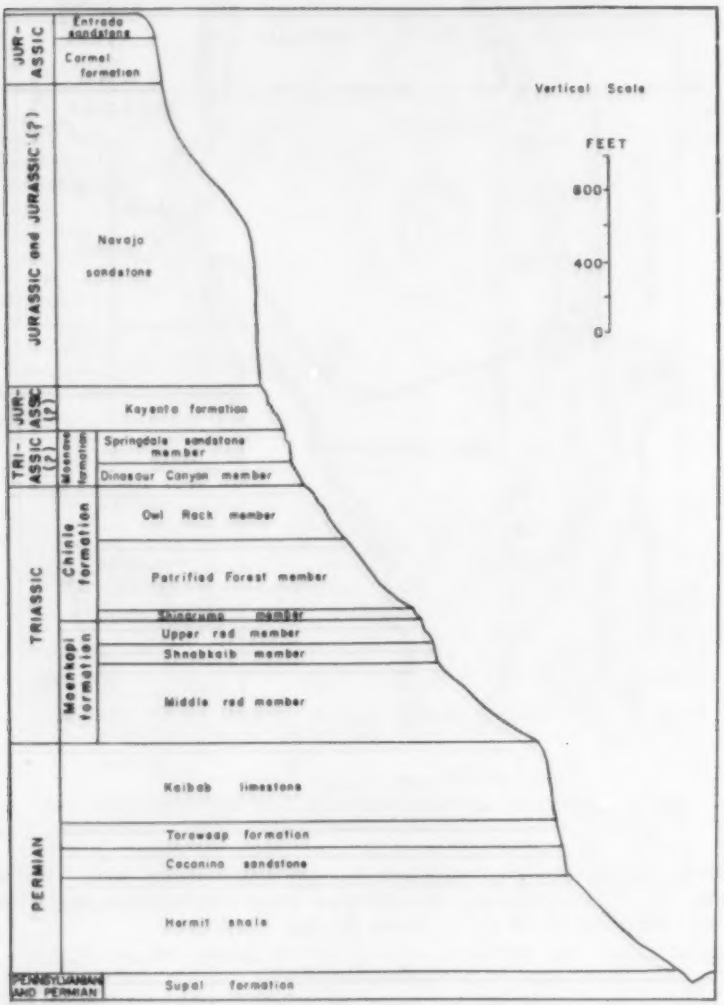

FIG. 2. Columnar section along east Vermilion Cliffs, Coconino County, Ariz.

includes rocks from the Supai formation of Pennsylvanian and Permian age to the Entrada sandstone of Jurassic age (Fig. 2). The faulted East Kaibab monocline in the western part of the area is separated from the Echo Cliffs monocline in the east by a gently folded structural terrace.

Most of the uranium deposits in the area occur in paleostream channels at or near the base of the Shinarump member of the Chinle formation. The Shinarump member ranges widely in thickness, areal extent, and composition. In channels the member is as much as 130 feet thick. In other places, perhaps only a few hundred feet from these channels, the Shinarump is absent. Where occurring as a persistent bed, it generally is 20 to 40 feet thick. The Shinarump ranges in composition from hard, well-cemented chert and quartzite conglomerate to poorly sorted sand and gravel. In places it is a clay-cemented crossbedded sandstone.

Sun Valley Mine.—Surface and drill hole data indicate that the Sun Valley mine is in a U-shaped bend of a paleostream channel filled with sediments of the Shinarump member. The channel is at least 1,000 feet long and 400 feet wide. In the deepest part of the channel, the Shinarump is about 130 feet thick and is composed of a basal bed of a chert- and quartzite-pebble conglomerate 40 feet thick overlain by 90 feet of crossbedded sandstone. The uranium deposits occur mostly in ellipsoidal shaped ore "pods," about 3 feet long and 2 feet wide, in the bottom 2 to 5 feet of the basal conglomerate. Since early in 1956, several hundred tons of uranium ore have been mined.

The only unoxidized uranium ore mineral identified from the Sun Valley mine is uraninite, which occurs as interstitial material and as rounded grains (up to 1 mm in diameter). Other minerals recognized are pyrite, sphalerite (light amber), hematite, and galena (rare). Although analysis of several samples showed a molybdenum content as high as 10 percent, no molybdenite has been identified, but there is possibly some jordisite. The jordisite was not identified in the samples, but is indicated by the abundance of the secondary molybdenum mineral, ilsemannite, which, according to Staples (11), forms more readily from jordisite than molybdenite. The possible difference between these latter two minerals is discussed by Staples. The cementing material in the conglomerate is calcite with minor chalcedony. The probable paragenetic sequence is: (1) uraninite (interstitial type), (2) pyrite, and (3) sphalerite. The secondary uranium minerals forming on the mine walls and on outcrops of the Shinarump are zippeite, a zippeite-like mineral, and an unnamed uranyl phosphate. In addition to these, ilsemannite is forming rapidly on the walls of the older mine workings. Carbonized wood and other carbonaceous material are found in the Shinarump member, but not necessarily associated with the uranium deposits.

RHENIUM

History.—In 1871, when Mendeleev constructed his chart of the elements, number 75 was one of the blank spaces which he predicted would be filled someday. His prediction did not come true until the year 1925, when the German chemists, Ida and Walter Noddack, first isolated the new metallic

element and named it rhenium. Little work was done with the metal from then until recently when studies in Germany and in the United States (principally at the University of Tennessee) have shown that rhenium and its alloys have excellent heat- and corrosion-resistant properties. Rhenium can be utilized for electric contact points, corrosion-resistance alloys, and in high temperature thermometry. Carlson (3) reports that a few hundred pounds of rhenium are produced annually. Meggers (6) refers to this element as a "new wonder metal," and states that "its remarkable properties insure increased concentration and extensive future application in science and industry."

Chemistry.—The known valences of rhenium are 1, 2, 3, 4, 5, 6 and 7, but valences of 4, 6, and 7 seem to be the more important ones. This property of assuming several valences make the element very sensitive to changes in redox conditions. The perrhenate ion ReO_4^- is more stable than the permanganate or perchlorate ions; it forms soluble compounds with many cations.

TABLE 1

RHENIUM CONTENT OF MOLYBDENITE[1]

No.	Source	Re, ppm	Reference
1	"U.S.A."	140	(5)
2	Climax, Colorado	28	(5)
3	Climax, Colorado	20	(2)
4	"Colorado"	1.8	(8)
5	McGill, Nevada	1030.	(2)
6	Miami, Arizona	152.	(2)
7	Miami, Arizona	150	(2)
8	Miami, Arizona	297	(2)
9	Miami, Arizona	688	(2)
10	"Canada"	20.4	(5)
11	Cananea, Mexico	120	(5)
12	"Peru"	36	(5)
13	"Bolivia"	0.05	(8)
14	"Finland"	18.	(5)
15	Norway	8	(5)
16	Norway, Flekkefjord	12.1	(5)
17	Norway, Hvaleroyene	90	(5)
18	Norway	1400	(5)
19	Norway, Stavanger	3040	(5)
20	Norway, Telemark	21	(8)
21	"Altenburg"	44	(5)
22	"Knabengruber"	13.3	(5)
23	"Mine di Gonnesfadiga"	19.8	(5)
24	"Bulgaria"	5.	(5)
25	Keskin, Turkey	50.	(5)
26	"Siberia"	0.6	(8)
27	"Japan"	10	(8)
28	Japan, Shirakawa	9.6	(5)
29	German East Africa[2]	2710.	(5)
30	Unknown	17.8	(5)
31	Unknown	3140.	(5)

[1] Prepared by Michael Fleischer, U. S. Geological Survey.
[2] Stated in another place to be "Southwest Africa."

The heptavalent rhenium compounds are practically limited to perrhenic acid, $HReO_4$, and its derivatives, including the anhydride, Re_2O_7, and certain sulfur and selenium compounds. The sulfides Re_2S_7 and ReS_2 are known.

Melaven (*7*) writes that there is considerable doubt as to the occurrence of rhenium as ReO_4, but the Re_2O_7 is common and is extremely soluble in water forming the acid $HReO_4$. The alkali and alkaline earth perrhenates are well defined white crystalline substances stable from room temperature to their melting points. $KReO_4$ is a rather insoluble salt (0.00494 g/ml at 2.0° C).

Rhenium has a naturally occurring radioactive isotope, Re^{187}, with a half-life of approximately 4×10^{12} years decaying to the osmium isotope, Os^{187}.

Association.—Rhenium and manganese belong to the same subgroup of the periodic system. However, rhenium is not closely associated with manganese in nature, but instead is found, in many places, associated with molybdenum. Noddack and Noddack (8), in their search for rhenium, have analyzed over 1,600 rocks and minerals. The only mineral they found to contain rhenium in appreciable amounts was molybdenite, 60 samples of which contained from 0.05 to 20 ppm rhenium. Since then, analyses of molybdenite have been published by Aminoff (1), Geilmann, and others (5), and Boyd and Larsen (2). All of these determinations are given in Table 1. The similarity of the ionic radii (9) of Mo^{4+}(0.68 kX) and Re^{4+}(0.56 kX) probably permits the replacement of molybdenum by rhenium in the molybdenite.

Noddack and Noddack also report minor amounts (less than 1.1 ppm) in the following minerals: clausthalite (PbSe), berzelianite (Cu_2Se), columbite ($(Fe, Mn)\ Nb_2O_6$), thortveitite ($Y_2Si_2O_7$), gadolinite ($(Fe,Be)_2Y_2Si_2O_{10}$), and alvite ($(Zr, Hf)\ SiO_4$). Geilmann (5) analyzed 9 wulfenites ($Pb\ MoO_4$) (including one from Mammoth Mine, Arizona, one from Red Cloud Mine, Yuma County, Arizona, and one from Bennett Mine, New Mexico) and found from 0.3 to 3.3 ppm rhenium.

Rankama and Sahama (9) report that the copper deposits in the Kupferschiefer in Mansfeld, Germany, contain molybdenite with a rhenium content of 0.01 percent; they also contain some uraninite.

According to Sargent (10), the only rhenium produced in the United States is extracted by the University of Tennessee from flue dusts obtained from the roasting of molybdenite ores at the Miami Copper Company's mill at Miami, Arizona.

Rhenium in the Sun Valley Mine.—Of the 29 samples from the Sun Valley mine analyzed for this study, all but 6 are from the Shinarump member of the Chinle formation within 4 feet of the contact with the underlying upper red member of the Moenkopi formation. Three samples, nos. 19, 28, and 29 (Table 2), are from the upper red member at the contact of Shinarump and upper red member. Samples 6, 16, and 17, are from a block of siltstone from the upper red member within the Shinarump member (Fig. 3) about 2 feet up from the contact. Analyses for 15 elements are included in Table 2. Of the other 54 elements looked for in the spectrographic analyses, some were

TABLE 2

SEMIQUANTITATIVE SPECTROGRAPHIC AND CHEMICAL ANALYSES (REPORTED IN PERCENT[1]) FOR 15 ELEMENTS IN 29 SAMPLES FROM THE SUN VALLEY MINE, COCONINO COUNTY, ARIZ.
Analysts: J. C. Hamilton—spectrographic; G. T. Burrow—chemical

Sample number	Laboratory number	Elements and lower limit of sensitivity														
		Re 0.005	U 0.05	Mo 0.0005	Ge 0.001	Dy 0.005	Er 0.005	Nd 0.01	Sm 0.01	Zn 0.02	Se (chemical)	Pb 0.001	Cu 0.0001	Co 0.0005	Ni 0.0005	Y 0.001
1	248137	0	7.	0.07	0.007	0	0	0	0	0.7	0.0001	.07	.03	.03	.03	.07
2	248138	0	0.07	1.5	0	0	0	0	0	0.15	0.00005	.15	.03	.03	.015	Tr
3	248139	0	1.5	0.15	<0.005	0	0	0	0	0.15	—	.07	.007	.015	.015	.03
4	248140	0	0.15	1.5	0	0	0	0	0	0.3	—	.15	.07	.03	.015	.003
5	248141	0.03	7.	0.3	0.007	0	0	0.03	0	1.5	0.0001	.15	.03	.015	.015	.03
6[3]	248142	0.007	0.15	0.7	0.003	0	0	0	0	0.07	—	.015	.003	.015	.007	.003
7	248143	0	0	0.03	0	0	0	0	0	0.03	—	.015	.003	.007	.003	.0015
8	248144	0	0	0.015	0	0	0	0	0	0	—	.03	.007	.015	.007	.0015
9	253035	0.007	0.07	0.7	0	0	0	0	0	0.3	—	.07	.015	.015	.007	.003
10	253036	0.015	0.07	0.7	0	0	0	0	0	0.07	—	.03	.015	.015	.007	.003
11	248564	0	0.07	1.5	0	0	0	0	0	0.07	—	.03	.015	.015	.007	.003
12	253037	0	0	0.007	0	0	0	0	0	0	—	0	.003	0	0	.003
13	253038	0	0	0.003	0	0	0	0	0	0	—	.003	.003	.0015	.0007	.0015
14	253039	0	0.03	1.5	0	0	0	0	0	1.5	—	.6	.03	.015	.007	.0015
15	253412	0.07	1.5	0.15	0.003	0	0.007	0.015	0.015	7.	0.0002	.07	.03	.015	.007	.07
16[2]	253413	0.07	0.7	1.5	<0.005	0	0	0.015	0.015	0.7	0.00005	.07	.015	.015	.03	.03
17[2]	253414	0	0	0.03	0	0	0	0	0	0	0.00005	.015	.007	.007	.007	.0015
18	253415	0	0.07	0.15	0	0	0	0	0	0.15	0.00005	.015	.03	.015	.007	.003
19[3]	253040	0	0	0.007	0	0	0	0	0	0	—	.0015	.007	.0015	.0007	.0015
20	254391	0.03	0.3	0.7	0	0	0	0	0	0.7	0.0001	.07	.03	.015	.015	.015
21	254392	0	0.15	0.3	0	0	0	0	0	0.3	—	.07	.03	.015	.007	.003

O—looked for but not detected (below limit of sensitivity).
M—major constituent; greater than 10 percent.

[1] For the spectrographic results figures are reported to the nearest number in the series 7, 3, 1.5, 0.7, 0.3, 0.15, etc. in percent. Sixty percent of the reported results may be expected to agree with the results of quantitative methods.

[2] From siltstone block of the upper red member of the Moenkopi formation within the Shinarump member of the Chinle formation (illustrated in Fig. 3).

[3] Siltstone from upper red member of the Moenkopi formation.

Samples not footnoted are from conglomerate from the Shinarump member of the Chinle formation.

TABLE 2—(*Continued*)

SEMIQUANTITATIVE SPECTROGRAPHIC AND CHEMICAL ANALYSES (REPORTED IN PERCENT[1]) FOR 15 ELEMENTS IN 29 SAMPLES FROM THE SUN VALLEY MINE, COCONINO COUNTY, ARIZ.
Analysts: J. C. Hamilton—spectrographic; G. T. Burrow—chemical

Sample number	Laboratory number	Elements and lower limit of sensitivity														
		Re	U	Mo	Ge	Dy	Er	Nd	Sm	Zn	Se (chemical)	Pb	Cu	Co	Ni	V
		0.005	0.05	0.0005	0.001	0.005	0.005	0.01	0.01	0.02		0.001	0.0001	0.0005	0.0003	0.001
22	254393	0.03	3.	0.3	0.007	0.03	0.015	0.07	<0.05	1.5	—	.03	.03	.03	.015	.15
23	254394	0	0.07	0.15	0	0	0	0	0	0.3	—	.015	.03	.03	.015	.0015
24	254395	0.07	3.	0.07	0.007	0.02	0.02	0.07	0	0.7	0.0001	.03	.015	.03	.015	.07
25	254396	0.015	M	0.07	0.007	0.02	0.01	0.07	0	0.7	—	.15	.03	.07	.15	.15
26	254397	0.015	M	0.15	0.015	0	0	0.15	0	1.5	0.0004	.07	.03	.07	.07	.15
27	254398	0	0.15	0.3	0	0	0	0	0	0.15	—	.07	.03	.015	.015	.003
28[3]	254399	0	0.03	0.007	0	0	0	0	0	0	—	.015	.015	.015	.015	.003
29[3]	254400	0	0	0.15	0	0	0	0	0	0	—	.003	.003	.007	.003	.003

0—looked for but not detected (below limit of sensitivity).
M—major constituent; greater than 10 percent.
[1] For the spectrographic results figures are reported to the nearest number in the series 7, 3, 1.5, 0.7, 0.3, 0.15, etc. in percent. Sixty percent of the reported results may be expected to agree with the results of quantitative methods.
[2] From siltstone block of the upper red member of the Moenkopi formation within the Shinarump member of the Chinle formation (illustrated in Fig. 3).
[3] Siltstone from upper red member of the Moenkopi formation.
Samples not footnoted are from conglomerate from the Shinarump member of the Chinle formation.

omitted from the table because they were either not significant to this study (e.g., Al, Si, etc.), absent in all samples (e.g., Hg, Li, Rh, etc.), or in nearly equal amounts in all samples (e.g., Yb, La, Tl, etc.). All analyses (except selenium) were made by a general semiquantitative spectrographic method, used to determine about 66 elements at a time and may therefore, be limited in the accuracy for certain elements. Because of this, no statistical methods have been used to reach conclusions. However, the authors believe that the following limited correlations and conclusions can be made by inspection of these analyses (29 samples):

(1) Eleven of the 29 samples contain from about 0.005 to 0.1 percent rhenium (limit of spectrographic sensitivity for rhenium is about 0.005 percent).

(2) A relationship between the rhenium and the molybdenum exists *only* in that when rhenium is present, the molybdenum content of the sample is relatively high (Table 2). However, several samples which contain equally high or higher molybdenum, have no rhenium.

(3) A much better relationship seems to exist between the rhenium and the uranium content. An increase in uranium usually accompanies an increase in rhenium. Although again there are several samples with a high uranium content but no rhenium.

(4) Some correlation can be seen in the rhenium-uranium-molybdenum-zinc relationship, but only to the extent that wherever rhenium is present, uranium, molybdenum, and zinc are present in amounts greater than 0.07 percent.

(5) The rare earths, dysprosium, erbium, neodymium, and samarium, are reported only in samples which contain rhenium, but not all of the rhenium-bearing samples contain these rare earths.

(6) Of the other trace elements, the only noticeable relationship is that with the exception of samples 1 and 3, the yttrium content is higher in the rhenium-bearing samples than in those which contain no rhenium.

(7) Chemical analyses for selenium on 10 of the samples (6 of them containing rhenium), ranged from 0.5 to 4.0 ppm selenium; the selenium content showed no relationship to the rhenium content.

In an attempt to isolate the rhenium or rhenium-bearing mineral, several mechanical separations were made. Two samples, nos. 22 and 24, containing respectively 0.03 and 0.07 percent rhenium, were disaggregated in water in an ultrasonic transducer. The samples were screened, and the -325 mesh fraction was filtered through a Seitz filter. Spectrographic analysis of the several fractions showed that the high rhenium values were in the -325 mesh filtrate. The filtrates from sample nos. 22 and 24 were evaporated to dryness, and the residues contained about 0.3 and about 1.5 percent rhenium, respectively. Except for particles less than half a micron in diameter which may have passed through the filter, these filtrates contained only that part of the sample which is soluble in hot water (about 90° C, from heat generated by the ultrasonic transducer). The filtrate of sample no. 24 contained about 72 percent

TABLE 3

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES (REPORTED IN PERCENT) OF RAW SAMPLE AND FILTRATE OF SAMPLE NO. 24 FROM SUN VALLEY MINE, COCONINO COUNTY, ARIZ. Analyst: J. C. Hamilton

Element	Limit of sensitivity	Raw sample	Filtrate	Step increase or decrease[1]
Mg	0.0005	0.15	3.	+4
Ca	0.005	7.	M	+2
Na	0.05	0.15	1.5	+3
K	0.7	0.7	3.	+2
Ti	0.0002	0.15	0.0015	−6
Mn	0.0002	0.07	0.7	+3
Co	0.0005	0.03	0.3	+3
Mo	0.0005	0.07	3.	+5
Nd	0.01	0.07	0	−2[2]
Ni	0.0003	0.015	0.3	+4
Pb	0.001	0.03	0	−4[2]
Re	0.005	0.07	1.5	+4
U	0.05	3.	1.5	−1
V	0.001	0.003	0.015	+2
Zn	0.02	0.7	3.	+2
Zr	0.001	0.015	0	−3[2]
Dy	0.005	0.03	0	−2[2]
Er	0.005	0.015	0	−2[2]

M—major constituent; greater than 10 percent.

0—looked for but not detected (below limit of sensitivity).

[1] Semiquantitative spectrographic analyses are reported to the nearest number in a series of steps (7, 3, 1.5, 0.7, 0.3, 0.15, etc. in percent). Sixty percent of the reported results may be expected to agree with the results of quantitative methods. With the exception of uranium, only those elements which show a two-step or greater increase or decrease are listed in this table.

[2] Indicate the number of steps down to the lower limit of sensitivity.

by weight of the total rhenium reported in the raw sample. It is not known whether further treatment of the raw sample with hot water would have extracted the remaining 28 percent rhenium, or if this percent represents an insoluble rhenium compound.

Table 3 shows a comparison of spectrographic analyses between the raw sample and the filtrate from sample no. 24. With the exception of the uranium, only those elements that showed a two-step or greater increase or decrease are listed in the table (semiquantitative spectrographic analyses are reported to the nearest number in a series of steps: 3, 1.5, 0.7, 0.15, etc., in percent). The elements (Mg, Ca, Na, K, Mn) which commonly form soluble chlorides and sulfates, are understandably greatly increased in the filtrate. Titanium and zirconium, which are often found in detrital minerals, and lead, probably in the form of galena in the raw sample, all show a decrease in the filtrate. The complete disappearance in the filtrate of the rare earths, dysprosium, erbium, and neodymium, indicate that they were probably contained in a detrital mineral (monazite?) in the raw sample. The zinc, cobalt, and nickel show an unusual increase in the filtrate. The relatively high percentages of rhenium, molybdenum, and uranium in the filtrate indicate the possible presence of a soluble rhenium-containing molybdenum mineral (ilsemannite?) and a soluble uranium mineral (zippeite?). Ilsemannite and

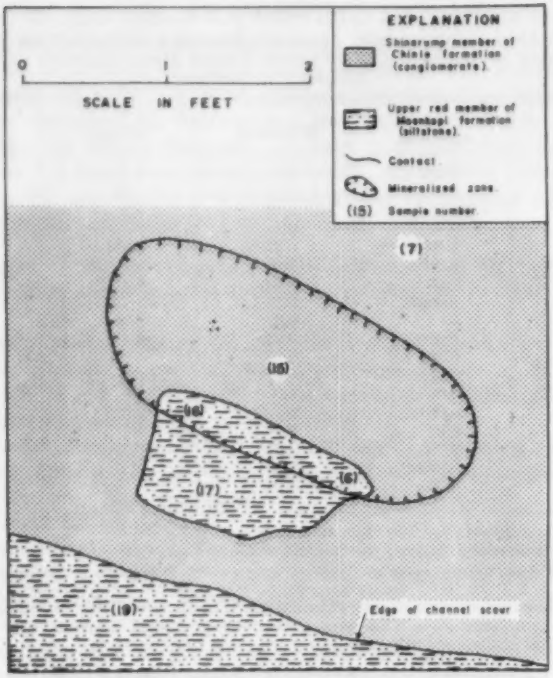

FIG. 3. Sketch of vertical section showing uranium ore "pod" and location of samples (analyses given in Table 4) in Sun Valley mine, Coconino County, Ariz.

zippeite are found in the Sun Valley mine but were not identified in sample no. 24. Positive qualitative tests for chloride and sulfate were obtained on sample no. 24.

The rhenium may also be in the form of the soluble oxide (Re_2O_7), which forms perrhenic acid ($HReO_4$) in water. This was first indicated by the difficulty experienced in attempting to evaporate to dryness the water-soluble filtrate from sample no. 24. A. D. Melaven (written communication, 1957) writes that "the dehydration of a water solution of $HReO_4$ at room temperature would result in a solution of gradually increasing viscosity as the solution became more concentrated in $HReO_4$." To prove further the presence of Re_2O_7, the rhenium-bearing (about 1.5 percent Re) water-soluble fraction of sample no. 24 was treated with acetone (Re_2O_7 is soluble in acetone) and filtered. After the acetone-soluble filtrate was evaporated to dryness, the residue (probably containing $HReO_4$) was heated on a steam bath in the presence of an excess of KCl. According to Druce (4), the reaction should

now be $HReO_4 + KCl = KReO_4 + HCl$. The solution was then cooled to 0° C to precipitate the relatively insoluble $KReO_4$ (4), and filtered. The precipitate, weighing 2.0 mg, contained greater than 10 percent rhenium, further confirming the presence of Re_2O_7 (or $HReO_4$ in solution) in the original water extract from sample no. 24.

Figure 3 shows a typical ore "pod" as found in the Sun Valley mine except that in this case the uranium mineralization has penetrated into a block of siltstone eroded from the Moenkopi formation and deposited with the Shinarump member of the Chinle formation (this block of siltstone probably broke away from the side of the stream channel during the deposition of the Shinarump). The color of the ore "pod" is black and the surrounding Shinarump member is light gray. Both the undisturbed upper red siltstone and

TABLE 4

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES (IN PERCENT[1]) FOR 23 ELEMENTS IN 6 SAMPLES FROM URANIUM ORE "POD" AND SURROUNDING ROCK IN THE SUN VALLEY MINE, COCONINO COUNTY, ARIZ.
Analyst: J. C. Hamilton

Element	Lower limit of sensitivity	Sample number[2] and laboratory number					
		Ore "pod"			Surrounding rock		
		15 253412	16 253413	6 248142	7 248143	17 253414	19 253040
U	0.05	1.5	0.7	0.15	0	0	0
Re	0.005	0.07	0.07	0.007	0	0	0
Mo	0.0005	0.15	1.5	0.7	0.03	0.03	0.007
Ti	0.0002	0.15	0.3	0.3	0.15	0.3	0.3
Mn	0.0002	0.03	0.015	0.015	0.07	0.003	0.07
Ba	0.0002	0.07	0.03	0.03	0.03	0.015	0.03
Cd	0.005	0.07	0.03	0	0	0	0
Co	0.0005	0.015	0.015	0.015	0.007	0.007	0.0015
Cu	0.0001	0.03	0.015	0.003	0.003	0.007	0.007
Gd	0.005	0.015	0.007	0	0	0	0
Ge	0.001	0.003	0.003	0.0015	0	0	0
Nd	0.01	0.015	0.015	0	0	0	0
Ni	0.0003	0.007	0.03	0.007	0.003	0.007	0.0007
Pb	0.001	0.07	0.07	0.015	0.015	0.015	0.0015
Tl	0.01	0.015	0.015	0.015	0	0	0
V	0.001	0.003	0.003	0.03	0.007	0.007	0.007
Y	0.001	0.07	0.03	0.003	0.0015	0.0015	0.0015
Zn	0.02	7.	0.7	0	0	0	0
Zr	0.001	0.007	0.07	0.03	0.015	0.03	0.03
Sr	0.0002	0.03	0.007	0.007	0.015	0.015	0.007
Sm	0.01	0.015	0.015	0	0	0	0
Dy	0.005	0	0	0	0	0	0
Nd	0.01	0.015	0.015	0	0	0	0

0—looked for but not detected (below limit of sensitivity).

[1] Semiquantitative spectrographic analyses are reported to the nearest number in the series 7, 3, 1.5, 0.7, 0.3, 0.15, etc. in percent. Sixty percent of the reported results may be expected to agree with the results of quantitative methods.

[2] See Figure 3 for location of samples.

the siltstone block (where not mineralized) are a light greenish gray, which suggests a bleaching from the normal dark brownish-red color of the upper red member.

Table 4 lists the analyses for 23 elements in 6 samples from the ore "pod" and surrounding rock shown in Figure 3. The common soluble-salt-forming elements (magnesium, calcium, sodium, and potassium) are present in all of the six samples (from 0.7 to 3.0 percent) but with differences too insignificant to be meaningful, and were, therefore, omitted from the table. The following observations are made from the inspection of Table 3:

(1) Rhenium is again found associated with uranium.
(2) Gadolinium, germanium, neodymium, and thallium are present only in the ore "pod" samples, but in percentages probably too close to the lower limits of sensitivity to be significant.
(3) Titanium, nickel, manganese, barium, cobalt, vanadium, zirconium, and strontium are present in amounts which are nearly equal in all samples.
(4) Uranium, rhenium, molybdenum, cadmium, lead, and zinc show a major increase in the ore "pod" samples along with a minor increase in the copper and yttrium content.

SUMMARY AND CONCLUSIONS

(1) Rhenium, in concentrations from about 0.005 to 0.1 percent, has been found in 11 of 29 samples from the Sun Valley mine and is associated with uranium and molybdenum (and probably with lead and zinc).

(2) The rhenium is concentrated up to about 1.5 percent in the hot-water-soluble (about 90° C) fraction of the samples, and is associated with water-soluble uranium and molybdenum.

(3) Further chemical tests, concentrating the rhenium up to greater than 10 percent, substantiate the theory that the rhenium in the Sun Valley mine is in the form of the oxide (Re_2O_7), or, if in water, the perrhenic acid ($HReO_4$).

(4) The rhenium may have been contained originally in the mineral jordisite. This is suggested by the association of the water-soluble molybdenum mineral, ilsemannite, with the rhenium oxide.

(5) The localization of the uranium, molybdenum, cadmium, lead, zinc, and rhenium in the siltstone block of the Moenkopi within the Shinarump member and in the adjacent Shinarump member of the Chinle formation (Fig. 3), indicates that these elements were probably deposited at the same time.

(6) The Sun Valley mine is the only uranium deposit on the Colorado Plateau known to contain any rhenium.

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THE SAMREID LAKE SULFIDE DEPOSIT, ONTARIO, AN EXAMPLE OF A PYRRHOTITE-PYRITE IRON FORMATION

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ABSTRACT

Many pyrrhotite and pyrrhotite-pyrite bodies, known to prospectors and geologists as "dikes," are being discovered in the Canadian shield as a result of intensive geophysical prospecting. The Samreid Lake pyrrhotite-pyrite body was chosen to serve as a type example for this kind of deposit.

The area in which the sulfide deposit occurs was mapped in detail to determine the lithological relationship between the sulfide and the country rock. In the northern part of the area the rocks are mostly amphibole-bearing and include amphibolites and amphibolitic tuffs with sporadic metatuffs and quartz siltites. These rocks are interbedded with minor flows. The southern part of the area is mostly underlain by metatuffs, quartz siltites and quartzites in which amphibole is sporadic or absent. The amphibolites, quartz siltites and quartzites have probably been formed from shale, and argillaceous siltstone and sandstone. The location of the mineralized quartzite, the host-rock of the sulfide body, roughly coincides with the contact between the amphibolitic and non-amphibole bearing rocks. The mineralized quartzite is recrystallized chert. Lava flows are interbedded with the sulfide-bearing quartzite. Diabase dikes intruded the rocks of the area.

The essential minerals making up the sulfide body are pyrrhotite and pyrite. Abundant magnetite is intergrown with the sulfides, marcasite is rare. Chalcopyrite and cubanite were noted in minor amounts. The sulfide body is essentially barren of base metal mineralization. Along part of the mineralized zone pyrite predominates, elsewhere pyrrhotite predominates or is the sole sulfide mineral. As a rule, however, pyrite and pyrrhotite occur together.

Magnetite is considered to have been precipitated in a marine environment. Deposition took place in an area of volcanic activity in which the clastic sediments were permeated by a gaseous network of H_2S. Locally precipitated iron hydroxide gels, and perhaps some magnetite, were converted to pyrite. At a post-geosynclinal orogenic stage in the history of the area pyrrhotite is considered to have formed at the expense of pyrite. Geological thermometry points to a temperature of formation of 420 to 600° C for these rocks. This temperature reflects post-depositional metamorphic conditions to which these rocks were exposed.

INTRODUCTION

General Statement.—Many pyrrhotite and pyrrhotite-pyrite bodies are being discovered in the Canadian shield as a result of geophysical investigations. These deposits, known to geologists and prospectors as "dikes," [1]

[1] The term "dike" is a field colloquialism; the deposits do not appear to be dikes as is apparent from a study of the Samreid Lake deposit.

FIG. 1. Index map.

show the interesting association of pyrrhotite, "a high temperature mineral not known to occur in ores of shallow or intermediate depths" (25, p. 830), with normal cherty iron formations.

"Pyrrhotite dikes" and pyrrhotite-pyrite deposits appear to be mostly devoid of base metal mineralization, in contrast to the rich pyrrhotitic deposits exemplified by Sudbury. The pyrrhotite-pyrite deposits, although generally valueless as a source of base metals, may serve as a source of sulfuric acid.

The Samreid Lake deposit was chosen as a type example for a pyrrhotite-pyrite body. The purpose of this paper is to describe the nature and occurrence of the deposit, and to discuss its origin.

Location and Accessibility.—The deposit is located in Township 157 in the Sault Ste. Marie Mining Division, District of Algoma, Ontario, about 28

airmiles NNE of the town of Blind River, and roughly half way between Sudbury and Sault Ste. Marie (Fig. 1). Floatplanes can land on Samreid Lake within a few hundred feet of the mineralized zones (Fig. 2).

A gravelled highway, the so-called White River Road, which connects with Highway 17 at Iron Bridge, passes within seventeen miles of the deposit. Talvey Metal Mines Ltd., the owner of the deposit, has bulldozed a road suitable for fourwheel drive vehicles with which to link the deposit with the highway.

The Quirke Lake uranium property of Algom Uranium Mines is about five airmiles southeast of the pyrrhotite-pyrite deposit.

Scope of Work.—An outcrop map of the area in which the deposit is located was made on the scale of 1" = 100 ft. About 4,700 feet of base line was cut in an east-west direction and about 70,000 feet of lines in a north-south direction. The field work was conducted during the summer of 1954 by the writer and his field assistant Mr. Charles Tritschler. A magnetometer survey was run concurrently with the geological survey by Mr. S. L. Spafford. A reconnaissance diamond drilling program involving a total of 5,000 feet followed the surveys. Ninety thin sections and two polished surfaces were examined under the microscope.

History of Prospect.—The deposit was discovered by Mr. Sam Bobowash, an Indian from Iron Bridge, Ontario, on November 1st 1935. Mr. Bobowash and his partner Sam Reid staked the property in October 1936 for the New Sudbury Prospecting Syndicate. Mr. Bobowash did considerable trenching exposing a limonite gozzan and highly mineralized pyrrhotite-pyrite zones. The property was considered a base metal prospect and rumor had it that assays gave up to 4% Cu, 2% Pb and 7% Zn, as well as gold and silver values. The deposit was staked by Harico Mining & Development Co. Ltd. in June 1954 and sold to Talvey Metal Mines, the present owner of the property.

Previous Work.—The area in which the deposit is located was mapped by Harding (17) on the scale of one inch to the mile. He made brief reference to the sulfide deposit. He noted (p. 9) that "in several localities west of Samreid Lake the Keewatin rocks have been replaced by massive sulfides consisting of pyrite, pyrrhotite, and a little chalcopyrite." He also reported (p. 10) the presence of galena and sphalerite in nearby scattered sulfide-bearing quartz veins and cautiously noted that "low gold and nickel values are reported to have been obtained."

AGE RELATIONSHIPS

The rocks underlying the mapped area (Fig. 2) are amphibolites, quartzites, tuffs, volcanic rocks and diabase. Harding (17, p. 4–5) assigned a Keewatin age to this rock assemblage and on his map (No. 48 k) showed a belt about 15½ miles long which he said was composed of Keewatin lavas, intrusives and sediments. The Keewatin rocks are considered by Harding to be intruded by Algoman granite which bounds this belt to the south, east and northeast. Rock assemblages of the type found in the Samreid Lake area have been called Keewatin on the basis of lithological resemblance to

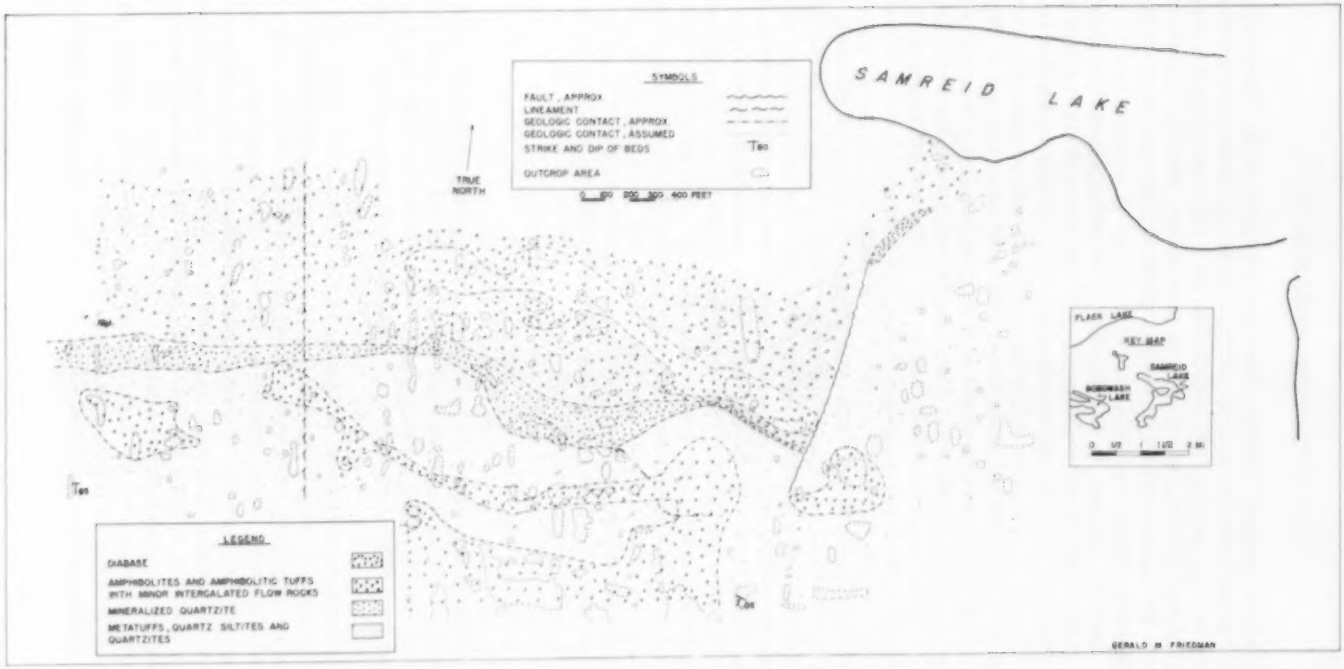

FIG. 2. Geologic map of Samreid Lake sulfide deposit.

Lawson's (24) original Keewatin located in the Lake of the Woods Region six hundred miles to the west of Samreid Lake. Although the practice of assigning a name with an age significance to a rock series on the basis of lithological equivalence alone has been accepted as standard procedure by numerous geologists working in the Canadian shield, modern stratigraphic concepts question such a practice.

The granites are said to be Algoman in accordance with the basic assumption that "one great revolution affected the whole shield and that most of the batholiths found throughout the shield were formed during this (Algoman) revolution" (16, p. 2). The general practice in stratigraphic correlation has been to assign a Keewatin, i.e., oldest Precambrian age, to "greenstones" of the type occurring in the area and to give an Algoman age designation to granites. By definition Algoman granite intruded Keewatin "greenstones." In reconnaissance field studies the writer has attempted to verify this generally stated age relationship but found no conclusive evidence to confirm it. Moreover, the "Keewatin" type rocks contain locally abundant quartzose sediments. If the "Keewatin" type rocks belong to the oldest part of the Precambrian and precede the granites, where is the source of the quartz for the quartzose and tuffaceous sediments? Since the only abundant quartz-bearing rock in the area is granite, the writer concludes that granite may be the source and formed the basement on which the sediments, tuffs and volcanic rocks were deposited. This interpretation does not necessarily mean that all of the granite in the area is older than the volcanics, as the granites may be of multiple age and origin. This reasoning upholds Gill's contention (op. cit., p. 4) that "the practice of labelling most granite batholiths Algoman, followed by some geologists, should . . . be abandoned." "Laurentian" granite which served as the source for Archean sediments probably is locally preserved, even though unrecognized.

GENERAL GEOLOGY

The rocks of the area are made up of metamorphosed pyroclastic rocks and sediments which are interbedded with lava flows (Fig. 2). The overall strike of the rocks is approximately east-west but locally there are marked deviations from this strike direction. The dip ranges from vertical to about 80° S.

In the northern part of the mapped area, the rocks are mostly amphibole-bearing and include amphibolites and amphibolitic tuffs with sporadic metatuffs and quartz siltites. They are interbedded with minor lava flows that range in composition from rhyolite to andesite. The southern part of the area is mostly underlain by metatuffs, quartz siltites and quartzites in which amphibole is sporadic or absent. A mineralized quartzite bed, the host-rock of the sulfide body, roughly coincides with the boundary between the amphibolitic and non-amphibole bearing rocks.

Nearly one fourth of the area mapped is underlain by diabase, which intruded all of the rock units in the area.

The geologic map of the area (Fig. 2) has been somewhat generalized

inasmuch as the amphibolitic and non-amphibole bearing rocks grade into each other and as it is locally difficult to differentiate between these two mapped units in the field. Moreover, amphibolitic rocks are interbedded in some places with non-amphibole bearing rocks and locally non-amphibole bearing rocks are intercalated between amphibolitic rocks.

Approximately east-west shearing is prominent in many outcrops of the mineralized quartzite unit, which thickens and thins along its strike. Narrow intercalated lava flows ranging in composition, from rhyolite to andesite occur within the area mapped as mineralized quartzite.

Near its eastern end the mineralized quartzite is displaced by a fault. The strike slip component of this fault is about 700 to 800 feet. A lineament in the western part of the mapped area, represented by a narrow north-south trending swamp zone, may be a joint or fault. No displacement along this structure was noted.

DESCRIPTIONS OF ROCKS

Amphibole-Bearing Metasedimentary Rocks and Tuffs (Amphibolites and Amphibolitic Tuffs). The amphibole-bearing metasedimentary rocks and tuffs are of dark greenish to black color and typically consist of quartz and amphibole. Quartz is the dominant mineral in some rocks whereas amphibole predominates in others. In some amphibolites, amphibole makes up more than 85 percent of the rock. Minerals present in subordinate amounts include biotite, epidote, chlorite, garnet, and feldspar. Accessory minerals are apatite, zircon, carbonate, scapolite, magnetite, leucoxene, pyrite and pyrrhotite.

The rocks have a grain-size range from very fine to fine and medium. In many of these rocks, quartz is very fine-grained in contrast to the coexisting amphibole which is medium-grained and locally coarse-grained. Rocks that are composed for the most part of amphibole are coarser-grained than those in which quartz predominates. In such rocks, small quartz grains form the matrix between large amphibole crystals, and many amphibole crystals diablastically enclose quartz grains. Amphibole shows, as a rule, blue to green pleochroic colors. Many amphibole crystals are elongated parallel to the bedding. Amphibole occurs in fine needles, ragged prisms or irregular anhedra, in some cases it is subhedral.

Feldspars, where present, are prominently embedded as phenocrysts in the quartz-amphibole matrix or make up part of this groundmass. The presence of feldspar phenocrysts imparts a porphyry appearance to these rocks. Minute particles of unidentified composition are distributed through many feldspar crystals and produce an intense clouding of the grains. Feldspar laths locally show partial replacement by epidote or chlorite. In some rocks subrounded quartz grains occur as phenocrysts in a quartz-amphibole matrix together with euhedral feldspar phenocrysts.

The amphibolitic rocks are cut by numerous quartz-chlorite-epidote veins and sporadic calcite-epidote veins.

Non-Amphibole Bearing Metasedimentary Rocks and Tuffs (Metatuffs, Quartz Siltites and Quartzites).—These rocks, in which quartz predominates,

are very fine-grained. Some rocks contain more than 75 percent quartz, which occurs in the form of tightly interlocked crystals and imparts a quartzite appearance to the rock. Others contain a sericite matrix, sporadic biotite, chlorite and epidote, or some carbonate grains and include feldspar and scapolite crystals. Interstitial biotite, chlorite, amphibole, epidote, and magnetite are locally present in minor amounts. Some of these rocks are essentially quartz-sericite intergrowths.

Porphyritic rocks contain feldspar phenocrysts and locally quartz phenocrysts and garnet porphyroblasts. These rocks are essentially composed of quartz and biotite or chlorite with subordinate muscovite, feldspar, scapolite, epidote, and garnet. Biotite sporadically occurs as porphyroblasts. Amphibole has been noted but is rare. Some rocks that are composed for the most part of tightly interlocked fine quartz grains resemble quartzite.

Bedding in thin section is manifested in some rocks by an alteration of fine to medium with very fine-grained bands. The very fine-grained bands locally contain a greater percentage of ferromagnesian minerals than the coarser bands. The long axis of biotite and many quartz grains shows a preferred orientation paralleling the bedding of the rock.

Mineralized Quartzite.—The quartzite is a very fine to fine or medium-grained rock which is typically monomineralic, but some quartzite samples studied contain an interstitial sericite matrix.

Flow Rocks.—The flow rocks include rhyolite, trachite, and andesite, some of which are porphyritic. In rhyolite porphyry, phenocrysts of potash feldspar occurring as stumpy rectangles are embedded in a biotite-amphibole matrix containing abundant quartz, subordinate sodic plagioclase, sporadic chlorite and epidote and accessory sphene. The phenocrysts enclose abundant embryo crystals of hornblende and epidote. Sparse calcite and epidote are contiguous with quartz. Rhyolites which are not porphyritic are composed of quartz, potash and soda feldspar, and amphibole, and locally biotite.

Quartz trachite is composed of alkali feldspar and amphibole with subordinate quartz (about 10%) and biotite. Accessory minerals include sphene and opaques. Andesite is essentially composed of lime-soda plagioclase and amphibole. Accessory minerals include epidote, quartz, and sphene.

A quartz andesite porphyry or dacite porphyry containing abundant blue quartz phenocrysts was identified in hand specimen.

Diabase.—The diabase is a metadiabase varying in grain-size from fine to medium and coarse, and is composed essentially of plagioclase and hornblende. This rock typically shows a diabasic texture. The feldspar crystals are normally euhedral and lath-shaped, but many feldspar crystals show signs of corrosion by the other minerals of the rock, and, are, as a rule, filled with numerous microlites of unidentified composition. Locally they carry minute crystals of epidote or hornblende and rarely chlorite, which have apparently been formed at the expense of the feldspar. Clear feldspars are not abundant although they are locally present. The occurrence of two plagioclase feldspars of different composition was noted but the composition was not determined. Hornblende generally occurs in ragged prisms or as irregular anhedra. It is of green or bluish color, and rarely mottled with brown

and green patches. Some hornblende appears to have replaced feldspar, but most has probably formed at the expense of pyroxene. Pyroxene was not observed in the rocks examined.

Epidote and chlorite are of sporadic occurrence. Epidote has preferentially replaced feldspar whereas chlorite has formed at the expense of hornblende. Chlorite is commonly intergrown with epidote; these two minerals appear to be genetically related. There is locally a very fine-grained intergrowth of feldspar and epidote. Near quartz veins the metadiabase is converted into an epidosite composed mostly of epidote but intergrown with variable amounts of chlorite.

Sporadic quartz is generally present; micropegmatite was noted in some samples. Some quartz grains occur as diablastic (sieve) inclusions in hornblende. A minor amount of biotite has been formed at the expense of hornblende. Accessory minerals include apatite, sphene, magnetite, pyrite, pyrrhotite and leucoxene.

Rocks that lack diabasic texture and are of very fine grain size may be classified as metabasalt. They are present in the area, but not abundantly, and on the map they are included with the diabases.

PREMETAMORPHIC NATURE OF SEDIMENTARY ROCKS AND TUFFS

The premetamorphic nature of many rocks is difficult or impossible to determine inasmuch as the mineralogy has been changed and diagnostic textures have been obscured or obliterated.

Amphibolites can be derived from a variety of rocks. The bedding in the amphibolites studied together with the presence of abundant very fine-grained quartz suggest derivation from a sediment, such as a shale or argillaceous siltstone. Porphyritic amphibolites have probably formed from tuffs, but "phenocrysts" of the type found in some of these rocks are also characteristic of Archean greywackes.

The porphyritic non-amphibole bearing rocks that are composed for the most part of tightly interlocked fine-grained quartz are probably metamorphosed acid tuffs. Some of the subrounded quartz phenocrysts in these rocks have the typical welded appearance of welded tuffs. Quartz siltites and quartzites may be argillaceous siltstones and sandstones.

The mineralized quartzite is an orthoquartzite in composition. Its intergrowth with abundant magnetite in a lava ("greenstone")-tuff-shale environment of the Archean type justifies the interpretation that it represents recrystallized chert, especially since quartz veins, in the rocks studied, show the characteristic texture of quartzite. Pettijohn (31, p. 960) notes that some of the rare pure "quartzite" occurrences reported from Archean rocks are probably recrystallized cherts. Teall (29, p. 640–642) and Pantin (28) describe the conversion of chert to quartzite as a result of metamorphism.

SULFIDE MINERALIZATION

The essential minerals making up the sulfide body are pyrite and pyrrhotite. Magnetite is abundantly intergrown with the sulfides. Examina-

tion of polished surfaces of two pyrrhotite samples showed enclosed porphyritic pyrite and idiomorphic grains of magnetite, and some secondary pyrite and marcasite that had apparently formed at the expense of pyrrhotite. Chalcopyrite and cubanite were noted in minor amounts. Nickel minerals and precious metals were looked for but were not found.

Abelson (1, p. 177) notes that the work of Arnold has shown a relationship between the *d* spacings for the (102) X-ray reflections and composition of synthetic pyrrhotites which are in equilibrium with pyrite. This method of obtaining pyrrhotite compositions is said to be (p. 178) as accurate as chemical analysis. The pyrrhotite composition of the Samreid Lake deposit can be determined from X-ray analysis, if the results of Arnold's study can be extended to natural pyrrhotite-pyrite mineral assemblages. Examination of a pyrrhotite-pyrite outcrop sample by X-ray diffraction, using quartz as internal standard, showed the presence of two pyrrhotites of different composition. The *d* spacings for the (102) X-ray reflections are respectively 2.062 and 2.054. According to Arnold's curve (1, p. 177) the two pyrrhotites contain 47.00 and 46.35 mol percent iron, respectively, corresponding approximately to formulas Fe_7S_8 and Fe_6S_7. A subsurface pyrrhotite from a drill-core showed the presence of three peaks for the (102) X-ray reflections. The *d* spacings are 2.062, 2.058 and 2.052 and correspond to 47.00, 46.70 and 46.20 mol percent iron, respectively.

Pyrite predominates or is almost exclusively present along part of the mineralized zone, whereas elsewhere pyrrhotite predominates or is the sole sulfide mineral. As a rule, however, pyrite and pyrrhotite occur together. On the surface the mineralized zone is weathered to a rust brown color and is leached to a depth of several feet.

Mineralization is confined to the quartzite indicated as mineralized quartzite on the geologic map (Fig. 2), or it occurs in flow rocks within ten feet of the contact with the quartzite. The mineralization ranges from sporadic to massive. Massive sulfide is composed of 90 to 95 percent pyrite and/or pyrrhotite. Veins and disseminations containing up to 40 percent pyrite intergrown with magnetite were found in the volcanics contiguous with the mineralized quartzite. Sulfides with or without magnetite occur in blobs, stringers, disseminations, veins, veinlets and ramifying networks, but where prominent they are massively interbedded with the quartzite. Pyrite or pyrite-pyrrhotite veins cut amphibole-magnetite bands. Pyrrhotite, enclosing small blobs of pyrite intergrown with magnetite occurs in fractures. Pyrite and calcite veins locally cut massive pyrrhotite. Pyrrhotite veins locally cut massive pyrite. Magnetite-rich bands alternate with magnetite-poor bands. Considerable chloritization is found near some of the strongly mineralized zones.

Some recorded percentage values of intergrown sulfides and magnetite contained in quartzite include magnetite 50 to 70 percent with pyrrhotite 30 to 50 percent, magnetite 40 to 50 percent with pyrite 50 to 60 percent, and magnetite 50 percent with pyrrhotite 30 and pyrite 20 percent. In many mineralized zones magnetite is absent or makes up less than 5 percent of the total metallic minerals present.

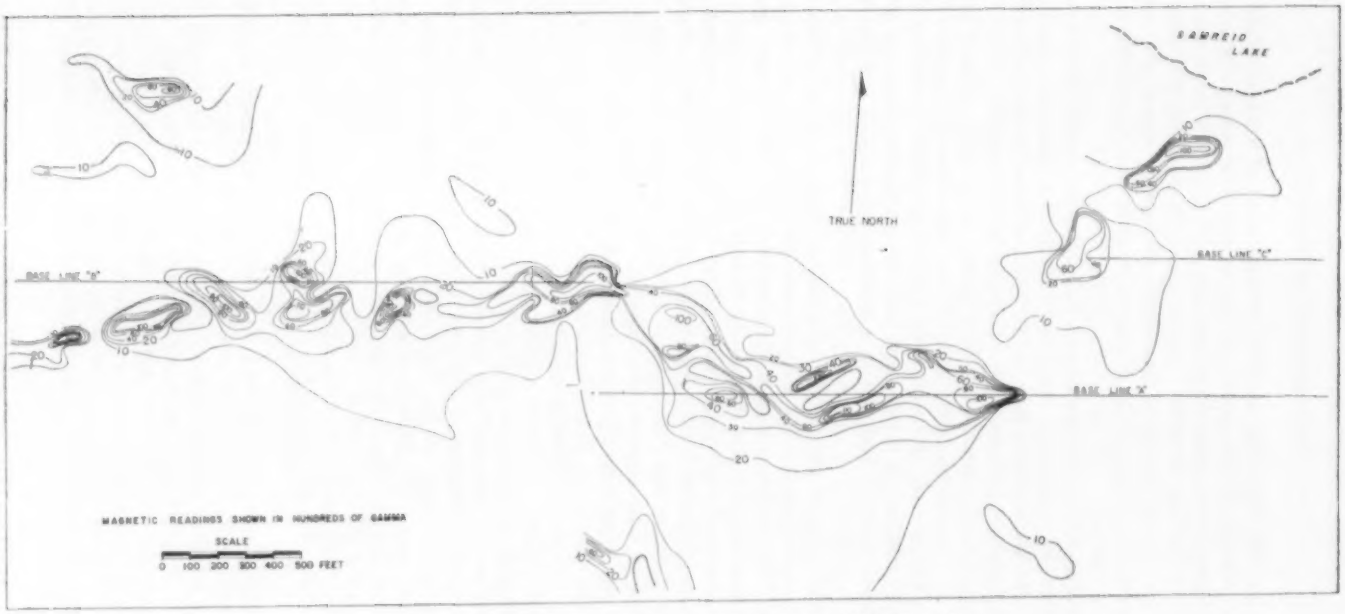

FIG. 3. Magnetic contour plat, Samreid Lake sulfide deposit.

The mineralized quartzite is cut by quartz veins and has been brecciated in places and filled with vein quartz, including euhedral quartz crystals. The quartzite contains abundant chloritic joint fillings with locally prominent pyrite mineralization. Diabase appears to have intruded the mineralized quartzite zone in places and to have been cut later by quartz and carbonate veins. Carbonate veins ½" thick enclose angular brecciated diabase fragments.

Alternating acid and basic flows, many of them porphyritic, are interbedded with the mineralized quartzite. Individual flows are usually thin, ranging in thickness from a few inches to a maximum of about forty to fifty feet. The majority are between five and twenty-five feet thick.

The mineralized quartzite has been traced for a total distance of about 3,300 feet by outcrop mapping (Fig. 2); a magnetometer survey (Fig. 3) indicated a total length of about 4,200 feet. The width of the unit termed mineralized quartzite on the geologic map ranges from 15 feet to 200 feet. This thickness includes both barren and mineralized zones and interbedded volcanics.

The true width of the sulfide zone ranges from about 55 to about 100 feet, in the central part of the mapped area where the mineralized quartzite is thickest. The width of the sulfide mineralization at the eastern end near the fault, decreases to about four feet. Where the mineralized quartzite is thickest, sulfur assays averaging about 42 percent have been obtained over a width of thirty-five feet (analysts: Bell-White Analytical Laboratories, Haileybury, Ontario and Union Assay Office, Salt Lake City, Utah).

Eighty-seven core samples were analyzed for copper, nickel, zinc, silver and gold. Four qualitative analyses were made for lead and two assays were run for cobalt (analysts: Bell-White Analytical Laboratories and Union Assay Office). Copper, where present, ranged from 0.08 to 0.21 percent, but many assays reported an absence of copper. Nickel was not found. Three assays indicated the presence of 0.10 to 0.31 percent zinc, but the others showed its absence. No lead was reported in the four samples analyzed for it. Cobalt assays indicated 0.022 and 0.058 percent in the two samples analyzed for it. A trace of silver was noted in every sample analyzed. Gold ranged from a trace to 0.055 ounce per ton, and was absent only in a few samples. The sulfide deposit is, therefore, essentially barren of base metal mineralization.

ENVIRONMENT OF DEPOSITION

The essential iron minerals occurring in the sulfide deposit include pyrrhotite, pyrite and magnetite. Pyrrhotite is generally regarded as a high temperature mineral, whereas pyrite and magnetite can form through a large temperature range. They can be of primary or diagenetic origin in sedimentary rocks, and they form at the high temperatures of igneous intrusives.

The lithologic association of the sulfide deposit is that of a normal magnetite iron formation as found elsewhere in the area, such as along Harding's (17, map 48k) Keewatin belt thirteen miles to the east in Township 145 and

in the Batchawana area described by Moore (27) and Friedman (15). Kilburn and Wilson (22) in their studies refer to similar deposits as normal iron formations. The modern investigators of the iron formations in the Lake Superior region (20, 35, 18, 19) state that the magnetite is original and of sedimentary origin. They discuss at length the considerable field, petrographic and experimental evidence and thermodynamic considerations which led them to this conclusion. Huber (18, p. 60–64) using thermodynamic data, introduced the stability field of magnetite into the original hematite-siderite-pyrite diagram of Krumbein and Garrels (23, p. 12). He showed (19) that magnetite is stable under mildly reducing conditions and at pH values of approximately 6 or above. This type of condition is characteristic for the slope zone that lies between the shallow wave and current swept shelf and the stagnant bottom areas of a restricted marine basin.

In the Samreid Lake deposit the lithology does not indicate a strongly reducing, anaerobic environment of deposition that is suggested by the stability field of pyrite. The activity of bacteria in the sulfur cycle as described by Schneiderhoehn (34, p. 256–259) may be partially responsible for the formation of sulfur-bearing gases, particularly H_2S leading to iron sulfide development, but the association with lava flows and tuffs emphasizes the action of volcanic exhalations. At Batchawana, one hundred miles to the northwest where similar geologic conditions prevail, pyrite and pyrrhotite occur in one of the iron formations studied by the writer. The sulfide content increases towards the contact with submarine volcanic rocks showing pillow structures. Sulfides locally make up as much as 30 percent of the rock over a width of twelve feet at the contact. At Samreid Lake, the volcanic activity accompanying the deposition of the lava flows and tuffs constituted the source for sulfur-bearing exhalations.

Submarine mofettes and thermal springs laden with H_2S are abundant in areas of submarine volcanic activity. Bernauer (7, 8, 9, 11) has shown at the island of Vulcano that H_2S plays a prominent role in sedimentation near submarine mofettes. Bernauer noted that large areas of unconsolidated and loosely-consolidated sediments are permeated by a gaseous network of H_2S with temperatures ranging from 25° to 100° C and in one boring he noted temperatures up to 500° C. Under such conditions locally precipitated iron hydroxide gels are converted to iron sulfides; similarly, magnetite may be converted to a sulfide. These types of reaction may have led to the formation of the sulfide mineralization at Samreid Lake. Bernauer (10) described the formation of iron sulfides at the present day in the tuff surrounding the volcano crater of the island of Volcano.

Collins, Quirke and Thomson (13, p. 73–78) relate the formation of pyrite in the Michipicoten iron ranges to hot springs and other solfatoric activity emanating from the underling volcanic rocks. Kilburn and Wilson (22) believe that the sulfides of iron formations were formed at the expense of magnetite and possibly from some of the iron-bearing silicates.

The great thickness of the "Keewatin" rocks in this area (a minimum of 5,000 to 6,000 feet) and the consanguineous association of tuff, shale, lava, and iron formations indicate deposition in a eugeosynclinal environment.

POST-DEPOSITIONAL CHANGES

The post-depositional history of the Samreid Lake sulfide deposit is manifested by two major events: 1. The intrusion of diabase, which cuts all of the rock units in the area, and 2. A regional post-diabase metamorphic cycle that affected both intrusive and intruded rocks. Both events may be related to an orogenic phase following eugeosynclinal development.

Pyrrhotite formation is probably related to the post-depositional history of the deposit. Its formation can be explained in one of two ways:

1. H_2S was not sufficiently abundant to precipitate a normal pyrite throughout all stages of deposition, and thus it gave rise to a gel or melnikovite pyrite, which contains less sulfur than normal pyrite. During a post-consolidation stage in the history of the area, the gel pyrite was converted to pyrrhotite as a result of higher temperatures. Typical melnikovite relict textures, however, were not noted in the pyrrhotite examined.

2. Iron sulfide was deposited as a normal pyrite. Pyrite was converted to pyrrhotite (pyrite $\rightarrow$ pyrrhotite + sulfur $\uparrow$) during a post-consolidation stage as a result of higher temperatures.

It should be noted, however, that the possibility of a primary origin for some of the pyrrhotite cannot be entirely ruled out. Rankama and Sahama (p. 187) state that pyrrhotite is "often connected with fumarolic activity." Allen et al. (4), give a minimum temperature of 80° at which pyrrhotite can be formed, and Ramdohr (32, p. 475), notes that pyrrhotite occurs in rocks that may not have been subjected to temperatures above 50° C. Erd, Evans, and Richter (14, p. 309) describe pyrrhotite that they consider to have been formed at temperatures between 25 and 40° C and at low pressure. These authors refer to thirteen other papers that report on the occurrence of low-temperature pyrrhotite in sedimentary rocks.

During folding and regional metamorphism mobilization of pyritic and pyrrhotitic material and magnetite probably gave rise to the sulfide and magnetite veins that cut the deposit and country-rock.

TEMPERATURE OF FORMATION

Attempts were made to use geological thermometry to arrive at a temperature of formation for the pyrrhotite-pyrite mineral assemblage. This task is complicated by the fact that metamorphism is superimposed on an igneous (volcanic) event.

The hornblende-plagioclase association, so typical of both the intrusive and intruded rocks of the Samreid Lake area, is characteristic of the amphibolite facies. Barth (5, p. 343) states that the maximum temperature attained in this facies appears to be around 500° C. In a later paper (6) Barth notes that "it is now textbook knowledge that this facies (amphibolite facies) corresponds to an approximate temperature range of 400–600° C."

The epidote-plagioclase association in these rocks serves as a geological thermometer (5, 1952, p. 286). Epidote is unstable in the amphibolite facies, except in the lower temperature range of this facies. The local replacement of plagioclase by epidote in the Samreid Lake rocks is a temperature indicator.

Although this thermometer is not yet accurately calibrated, Barth (5, p. 286) notes that under a pressure of around 1,000 atmospheres (corresponding to a depth of about 3 to 4 km) the upper limit of epidote formation at the expense of plagioclase is about 450° C. The replacement of plagioclase by epidote has not progressed beyond the initial stages in the Samreid Lake rocks. The estimated grade of metamorphism of the Samreid Lake rocks is equivalent to the lower temperature range of Barth's amphibolite facies near the boundary with the epidote amphibolite facies.[2] The lithology of the rocks indicates a post-depositional temperature of about 450° C. However, according to Winkler (36, p. 67) the lower boundary of the amphibolite facies lies in the temperature range of 525 to 560° C.

Cubanite that occurs in pyrrhotite as an intergrowth with chalcopyrite can be used as a geological thermometer. It requires a minimum temperature of formation of 250° C (32, p. 385). McKinstry and Kennedy (26, p. 381) note that cubanite intergrown with either chalcopyrite or pyrrhotite presumably represents "unmixing of a solid solution stable above 400 to 500 degrees." They continue "in ores presumably formed at lower temperatures, pyrrhotite and chalcopyrite occur together but cubanite is usually lacking." Ramdohr (33, p. 482), however, notes that formation of cubanite takes place at a temperature range of 250–300° C and that former estimates of temperatures up to 450° are much too high.

TABLE 1

GEOLOGICAL THERMOMETRY FOR PYRRHOTITE-PYRITE IRON FORMATION

Minerals or experiment	Temperature of formation
Epidote-plagioclase relation	450° C (Barth), 525–565° C (Winkler)
Pyrrhotite-pyrite relation	420, 480, 565, 600° C (method of Arnold)
Cubanite-chalcopyrite relation	400–500° C (McKinstry and Kennedy)
Decrepitation experiment	400–500° C (Kilburn)

Abelson (2, p. 194) in referring to the study of Arnold states that the composition of pyrrhotite when coexisting in equilibrium with pyrite is a function of temperature and pressure. This geological thermometer is valid only (p. 195) in deposits containing no more than small amounts of cobalt and nickel. As the Samreid Lake deposit lacks nickel and contains only a trace of cobalt, the curves of Arnold (p. 194) for determining the temperature of formation can be utilized. Two pyrrhotites of a Samreid Lake outcrop sample, determined by x-ray analysis, contain 46.35 and 47.00 mol percent iron which corresponds to a temperature of formation of 565 and 420° C, respectively, at a pressure of 1,000 bars (roughly equivalent to a depth of 3 to 4 km). Three subsurface pyrrhotites contain 46.20, 46.70 and 47.00 mol percent iron which corresponds to a temperature of formation of 600°, 480° and 420° C, respectively, at a pressure of 1,000 bars.

Kilburn (21) used liquid inclusion decrepitation experiments on pyrrhotite "dikes" of the Northwest Territories to determine the temperature of

[2] The appearance of epidosite and locally abundant chlorite is largely restricted to later quartz veins and, therefore, is not pertinent to this discussion. Some of the chlorite and muscovite may be the result of retrograde metamorphism.

formation. He arrived at a temperature of about 400 to 500° C. The estimated grade of metamorphism of Kilburn's rocks is very similar to that of the Samreid Lake rocks.

Table 1 summarizes the results of geological thermometry. Although the validity of individual methods of thermometry may be disputed, taken collectively a temperature of formation of 420 to 600° C is indicated for these rocks. This temperature probably reflects the post-depositional metamorphic conditions to which the rocks were exposed.

ARE PYRRHOTITE-PYRITE DEPOSITS NECESSARILY BARREN OF BASE METAL MINERALIZATION?

Kilburn and Wilson (22) state that pyrrhotite iron formations are barren of other base metal mineralization. The present investigation seems to bear out this conclusion for the Samreid Lake deposit. Pennington and Davis (30) describe similar deposits from Minnesota and Alcock (3) and Byers (12) from Saskatchewan, which are also devoid of base metal mineralization. All of these deposits, which are restricted to the Canadian shield, are pyrrhotite or pyrrhotite-pyrite iron formations with a high sulfide content. These deposits belong to the "submarine exhalative sedimentary ore body type" of Schneiderhoehn (34, p. 179–183) to which a mode of origin similar to that interpreted for the Samreid Lake deposit is ascribed. These submarine exhalative sedimentary ores commonly are of complex mineralogy and include important copper-lead-zinc deposits, such as Rammelsberg in Germany (32, 1953), Mount Isa in Queensland, Australia (34, p. 263), and Consolidated Sudbury Basin in Ontario. For the Rammelsberg deposits Ramdohr (32) has convincingly shown that the submarine exhalative mechanism is capable of giving rise to large base-metal sulfide deposits. The striking difference between the productive base-metal deposits and the pyrrhotite or pyrrhotite-pyrite iron formations among others, is, the very simple mineralogy of the pyrrhotitic rocks and the minor pyrrhotite content of the base metal deposits. The question arises: why are these pyrrhotitic deposits barren whereas other sulfide deposits of similar geology and origin are base metal producers? Although cognizance should be taken of this important question, no solution is offered here. More facts pertaining to the geology of other pyrrhotitic deposits are needed, as well as additional information on the geochemistry of pyrrhotite.

CONCLUSIONS

The Samreid Lake sulfide deposit was chosen as a type example of a pyrrhotite-pyrite iron formation. Its geology is summarized as follows:

1. The rocks of the area are made up of metasediments and pyroclastic rocks which are interbedded with lava flows. In the northern part of the area mapped, the rocks are mostly amphibole-bearing and include amphibolites and amphibolitic tuffs with sporadic metatuffs and quartz siltites. These rocks are interbedded with minor lava flows. The southern part of the area

is mostly underlain by metatuffs, quartz siltites and quartzites in which amphibole is sporadic or absent. A mineralized quartzite bed, the host-rock of the sulfide body, roughly coincides with the boundary between the amphibolitic and non-amphibole bearing rocks.

2. The amphibolites, quartz siltites and quartzites have probably been formed from shale, and argillaceous siltstone and sandstone. The mineralized quartzite is recrystallized chert.

3. Nearly one-fourth of the area mapped is underlain by diabase, which intruded all of the rock units in the area.

4. The essential minerals making up the sulfide body are pyrite and pyrrhotite. Magnetite is abundantly intergrown with sulfides. Secondary pyrite and marcasite have apparently been formed at the expense of pyrrhotite. Chalcopyrite and cubanite were noted in minor amounts.

5. The mineralized quartzite has been traced for a total distance of about 3300 feet by outcrop mapping; a magnetometer survey indicated a total length of about 4200 feet.

6. The true width of the sulfide zone ranges from about 55 to 100 feet in the central part of the mapped area where the mineralized quartzite is thickest. The width of the mineralization decreases to about 4 feet. Where the mineralized quartzite is thickest, sulfur assays averaging 42 percent have been obtained over a width of thirty-five feet.

7. The sulfide deposit is essentially barren of base metal mineralization.

The inferred environment of deposition is summarized as follows:

1. Magnetite accumulation took place in a marine environment, probably on the slope zone of a shallow sea in an area of submarine volcanic activity.

2. Volcanic activity included the discharge of tuffs and the outpouring of lava.

3. Iron hydroxide gels and perhaps some magnetite were converted to pyrite by the action of H_2S that permeated the clastic sediments.

4. Diabase was injected after consolidation of sediments and the volcanic flows and tuffs.

5. A regional post-diabase metamorphic cycle affected the rocks of the area. Temperatures up to 420–600° C were reached during the metamorphic stage and pyrrhotite probably formed at the expense of pyrite.

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THE CHEMICAL COMPOSITION OF MINNESOTA LAKE MARL —COMPARISON OF RAPID AND CONVENTIONAL CHEMICAL METHODS

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ABSTRACT

Chemical analyses of nine samples of marl from lakes in Minnesota by conventional analytical procedures and by modified or rapid methods that make use of ethylenediamine tetraacetic acid, EDTA, are compared. The two procedures report the composition in somewhat different terms. In the rapid analysis the sodium carbonate fusion for decomposition of the sample is eliminated. Insoluble material rather than SiO_2 is reported; Al_2O_3 is replaced by a difference value, M_2O_3. Results for CaO, MgO, and CO_2 are comparable to the conventional gravimetric determinations.

The Minnesota lake marl is composed chiefly of calcium carbonate with admixed silt, sand, and organic matter. The organic matter complicates the analytical procedures and is removed by ignition of the sample. Ferrous iron and total water cannot be determined. The analyzed samples range from 0.5 to 17 percent in SiO_2 content and from 31 to 51 percent in CaO. The MgO content is small, ranging from 1.1 to 1.8 percent.

The rapid analysis, although designed for Minnesota lake marl, can be applied to other carbonate materials. It has the advantage of permitting a large number of samples to be handled.

INTRODUCTION

THE marl deposits of the Minnesota lakes are composed chiefly of calcium carbonate with varying amounts of admixed material, largely silt and organic

matter. Although the clay content is small or negligible, the term marl has been used for these unconsolidated lake deposits largely for lack of a better name. The deposits are of potential value for Portland cement, agricultural lime, and other applications. Earlier investigations by Thiel (6) located most of the known deposits and gave data on their extent and approximate composition. Recent studies of some of the deposits by the Minnesota Geological Survey for the Iron Range Resources and Rehabilitation Commission required a large number of chemical analyses. Simple procedures were needed to give reliable figures for CaO and to provide information on as many other constituents as possible. For this purpose, standard analytical procedures were modified to make use of the versatile reagent ethylenediamine tetraacetic acid, EDTA, and the rapid chemical methods here described were thus developed.

Chemical analyses (Table 1) of nine selected samples were made by the conventional analytical procedures of the Rock Analysis Laboratory to give

TABLE 1

CHEMICAL ANALYSES OF MARL
(Conventional Methods)

	1	2	3	4	5	6	7	8	9
SiO_2	.43	2.82	6.19	10.11	7.80	9.63	14.40	13.34	16.88
Al_2O_3	.11	.42	.13	.06	1.17	.15	1.50	1.96	2.15
Fe_2O_3	.24	.73	.44	.35	.82	.71	1.14	1.52	2.43
TiO_2	.00	.03	.01	.02	.06	.03	.08	.11	.13
P_2O_5	.03	.03	.02	.12	.05	.15	.11	.12	.14
Na_2O	.03	.07	.04	.07	.19	.07	.28	.23	.30
K_2O	.00	.07	.02	.04	.18	.06	.30	.34	.39
CaO	51.61	49.13	47.36	42.39	42.34	41.56	39.96	39.56	30.82
MgO	1.23	1.50	1.32	1.45	1.11	1.54	1.81	1.40	1.79
MnO	.13	.23	.18	.28	.10	.16	.15	.19	.19
CO_2	41.66	39.93	38.23	34.50	33.70	33.66	32.64	32.30	25.00
SO_3	.60*	.57	.40	.73	1.13*	.44	.97	.62	.74
H_2O^-	.54	.73	1.11	1.62	1.52	1.68	1.09	1.48	2.78
Ignition**	3.41	3.81	4.38	8.06	9.70	9.95	5.42	7.23	16.18
	100.02	100.07	99.83	99.80	99.87	99.79	99.85	100.40	99.92

* Figures from Table 2. ** Total loss on ignition minus CO_2 and H_2O^-.

1. Rat Lake, Hubbard Co. (Sec. 8, T144N.R34W), Station 5 on west shore of lake; taken at depth of 17.5–18.2 feet; Cat. No. HR 5–7.

2. Warner Lake, Stearns Co. (Sec. 33, T123N.R27W), dry lakeshore deposit; large sample taken for Univ. Minn. Mines Experiment Station; Cat. No. R 2235.

3. Warner Lake, Stearns Co., large wet sample from lake taken for Univ. Minn. Mines Experiment Station; Cat. No. R 2334.

4. North Twin Lake, Hennepin Co. (Sec. 3, T118N.R21W), Station 7 in SW part of lake; taken at depth of 12.5 feet; Cat. No. T-50.

5. Nisswa Lake, Crow Wing Co. (Sec. 8, T135N.R29W), composite of 18 holes in SW part of deposit; Cat. No. CNC 1-S.

6. Warner Lake, Stearns Co. (Sec. 33, T123N.R27W), Station 1, north shore of lake; taken at depth 12.5–13.3 feet; Cat. No. W-9.

7. Fuller Lake, Stearns Co. (Sec. 34, T123N.R27W), Station N on northern shore of lake; taken at depth of 22–22.8 feet; Cat. No. F-5.

8. Fuller Lake, Stearns Co., Station on northern shore of lake; taken at depth of 22.5–23.3 feet; Cat. No. F-34.

9. Fuller Lake, Stearns Co., composite of 6 holes; Cat. No. R 2241.

TABLE 2

PROXIMATE CHEMICAL ANALYSES
(EDTA and Rapid Methods)

	1	2	3	4	5	6	7	8	9
Insoluble	.51	3.07	6.24	9.96	8.57	9.65	15.52	14.09	18.21
M_2O_3	.11	.30	.31	.40	1.18	.62	1.38	2.32	2.12
Fe_2O_3	.25	.70	.41	.30	.78	.64	1.02	1.42	2.22
CaO	51.69	49.07	47.36	42.39	42.41	41.59	39.93	39.50	30.74
MgO	1.23	1.50	1.49	1.47	1.05	1.55	1.85	1.41	1.71
MnO	.13	.24	.19	.28	.11	.16	.16	.19	.21
CO_2	41.83	39.70	38.27	34.57	33.69	33.44	32.54	31.88	25.05
SO_3	.60	.57	.41	.77	1.13	.48	.99	.70	.76
H_2O^-	.57	.65	1.06	1.62	1.57	1.58	1.14	1.48	2.62
Ignition	3.19	3.98	4.38	7.99	9.65	10.26	5.56	6.91	16.13
	100.11	99.78	100.12	99.75	100.14	99.97	100.09	99.90	99.77

Location of samples given in Table 1.

detailed chemical information as to the composition of Minnesota marl, and to provide reference samples for testing the rapid methods (Table 2). Results obtained by the two procedures, the standard or conventional chemical analysis and the rapid or abbreviated analysis, are compared. The two procedures report composition in somewhat different terms. The rapid methods give values for moisture (H_2O-), loss on ignition, insoluble material, M_2O_3, Fe_2O_3, CaO, MgO, CO_2, and total sulfur, reported as SO_3. No provision is made for determining titania, because this constituent divides unpredictably between the insoluble material and the ammonia group, here referred to as M_2O_3. As reported in the rapid analyses, M_2O_3 includes those oxides precipitated by ammonia in the filtrate from the insoluble material, less Fe_2O_3.

In the discussion that follows the usefulness and the limitations of the rapid methods are considered. The rapid procedures are described in some detail, and although they are directed to the analysis of Minnesota lake marl, they can be applied with little modification to other carbonate materials. No special equipment is needed, other than that found in most analytical laboratories, and the complete analysis can be made with porcelain in place of platinum crucibles.

The acid-insoluble material in the marl is largely silica in the form of silt-size quartz grains and fresh-water diatom tests. Small amounts of silicates, including microcline, plagioclase, epidote, hornblende, garnet, and zircon, are present, as well as hematite, magnetite, rutile, leucoxene and other minerals. The feldspars account for the sodium and potassium reported in the analyses (Table 1). Procedures designed to break up the insoluble silicates and so yield a precise figure for SiO_2 were considered, but unavoidably they lead to a much more lengthy analysis. Such a refinement does not appear to be worthwhile, because the discrepancies between figures for insoluble material and SiO_2 (Table 3) are not unduly large, except in marl of low grade.

The marl samples were taken in the field with hand samplers. They were

TABLE 3

INSOLUBLE MATERIAL AND SiO_2; M_2O_3 AND Al_2O_3

Sample	Insoluble material	SiO_2	M_2O_3[1]	Al_2O_3
1	0.51	0.43	0.11	0.11
2	3.12 3.01	2.82	.30	.42
3	6.19 6.29	6.19	.30 .31	.13
4	9.96	10.11	.40	.06
5	8.57	7.80	1.18	1.17
6	9.74 9.62 9.60	9.63	.62 .62	.15
7	15.52	14.40	1.38	1.50
8	14.08 14.09	13.34	2.32 2.31	1.96
9	18.27 18.16	16.88	2.11 2.14	2.15

[1] Ammonia group less Fe_2O_3.

split in the laboratory, and the portion used for chemical analysis was air dried and ground to pass an 80-mesh screen. Samples were thoroughly mixed by hand rolling on light-weight paper.

CONVENTIONAL METHODS

The chemical procedure, largely gravimetric, of the University of Minnesota Rock Analysis Laboratory was used with some minor modifications. After determination of moisture and loss on ignition in a platinum crucible, the sample is mixed with sodium carbonate and sintered. Silica is determined after separation by hydrochloric acid dehydration followed by volatilization with hydrofluoric acid, and the residue is fused with a little carbonate and added to the filtrate from the silica. The ammonia group is separated by double precipitation as usual, weighed, fused with pyrosulfate, and dissolved in 5–10 percent sulfuric acid. Following the colorimetric determination of titanium in this solution with peroxide, total iron is titrated potentiometrically with dichromate after reduction with stannous chloride. Organic matter in the marl precludes determination of ferrous iron, and total iron as Fe_2O_3 is reported in all analyses. Al_2O_3 is determined by difference.

Manganese, calcium, and magnesium are precipitated successively in the filtrate from the ammonia precipitate, using persulfate, oxalate, and phosphate. Manganese is then determined colorimetrically after periodate oxidation, calcium is ignited to the oxide and weighed, and magnesium is weighed as

pyrophosphate. The small amounts of calcium and manganese in the $Mg_2P_2O_7$ are recovered and the appropriate corrections made.

Phosphorus, sulfur, and carbon dioxide are determined on separate samples by conventional gravimetric methods. Sodium and potassium are extracted as chlorides by the J. Lawrence Smith method, converted to sulfates and determined by flame spectrophotometry.

RAPID METHODS

General Statement.—Moisture and loss on ignition are determined on a 1-gram sample which is weighed into a Coors No. 1 porcelain crucible with a tightly fitting cover. Porcelain crucibles can be used with most samples for all ignitions and weighings with little or no loss of precision if certain precautions are taken. Crucibles were pretreated by filling them half full of finely powdered marl and igniting 3–4 hours in the muffle. After this treatment, which removes the inner glaze, they change very little in weight throughout an analysis. After ignition, porcelain crucibles should be permitted to remain in the desiccator long enough to come to room temperature before weighing. This may require 2 hours or more if several large crucibles are put in the same desiccator.

The ignited marl is transferred to a 250 ml Pyrex beaker, and treated with dilute hydrochloric acid, then evaporated to dryness. The residue is taken up with a little acid, and SiO_2 and insoluble matter are removed by filtration. Although casseroles are usually recommended for the dehydration of silica (1), beakers serve equally well and are more convenient to handle.

The filtrate from the insoluble material is made up to volume, and half of it is taken for the determination of M_2O_3, CaO, MgO, and sulfur. Smaller aliquots are taken for the determination of manganese and iron, and an aliquot for the direct determination of calcium may also be taken at this stage. Attempts to determine MgO by complexometric titration before separation of the ammonia group were not successful because of the interference of aluminum.

After separation of the ammonia group, the filtrate is made up to volume, and aliquots are taken for the determination of calcium, calcium plus magnesium, and sulfur. A correction for manganese is not usually required; however, precipitation of manganese with the ammonia group using bromine, or its separation by means of persulfate, may be advisable if large amounts are present.

The great advantage of the procedure outlined above lies in the use of a single sample for all determinations except that of CO_2. Because the marl contains organic matter which must be removed by a time-consuming ignition, the single sample expedites the analysis.

The methods for CaO, MgO, and Fe_2O_3 are based on those described by Cheng, Kurtz, and Bray (3), except that calcein is used for the calcium titration (4). The voluminous literature on EDTA methods is well abstracted and summarized by Barnard, Broad, and Flaschka (2) and by Welcher (8).

PROCEDURE

Moisture.—Weigh a 1-gram sample of the air-dried marl into a porcelain crucible which has been pretreated as described above. Dry at 105–110° C in an electric oven overnight, cool for 2 hours in a desiccator, and weigh. Marl samples often continue to lose weight even after 12 hours. In part this may be due to loss of absorbed water or to partial destruction of organic matter. The prescribed conditions are somewhat arbitrary.

Loss on Ignition.—Place the crucible, uncovered, in the cold muffle and bring slowly to red heat to burn off organic matter and oxidize sulfur. Cover, and heat to 750° for 3–4 hours. Allow the crucible to cool to dull red in the muffle before transferring to the desiccator, and allow 2–3 hours before weighing.

Insoluble Material.—Carefully transfer the contents of the crucible to a 250 ml beaker, using first water and then a few drops of 1 : 1 hydrochloric acid. Add 10 ml of concentrated hydrochloric acid. Evaporate to dryness on the steam bath, breaking up lumps of silicic acid with a glass rod. Transfer to a hot plate and bake to remove acid and dehydrate the silica. The surface temperature of the hot plate should be under 200° C. If much magnesium is present, plate temperature should not exceed 120° C (1).

When dry, cool, and add to the residue 2.5 ml of concentrated hydrochloric acid, keeping the beaker covered. Allow to stand for 10–15 minutes, then add 25–30 ml of water and boil 2–3 minutes. Filter at once through a 7 cm Schleicher and Schuell white ribbon or Whatman No. 40 paper, catching the filtrate in a 100 ml volumetric flask. Wash first with a little 1:20 hydrochloric acid, then with hot water to a volume of about 90 ml. Reserve the filtrate, delaying the dilution to volume until ready for the pipetting operation.

Ignite the insoluble material at the same temperature as was used for loss on ignition, and weigh.

M_2O_3 Group.—Dilute the filtrate from the insoluble material to 100 ml and aliquot as follows:

1. 50 ml for M_2O_3 group (250 ml beaker)
2. 10 ml for Fe_2O_3 (200–250 ml conical flask).
3. 10 ml for MnO (150 ml beaker)
4. 10 ml for CaO (200–250 ml conical flask).

Boil the 50 ml aliquot for 3–4 minutes to remove CO_2. Add 3 ml of ammonium chloride solution (150 g/l) and precipitate with ammonia at pH 6.2–6.5. The pH is determined using nitrazine indicator paper in conjunction with methyl red. The very small squares of nitrazine paper added contribute negligible contamination. Filter and wash with hot 2 percent solution of ammonium chloride. Scrub the beaker and transfer the precipitate to the filter. The filtrate and washings are caught in a 100 ml volumetric flask. Ignite the precipitate and weigh; subtract the total iron as Fe_2O_3 and report M_2O_3.

Total Iron.—To the aliquot reserved for the purpose add about 0.02 gram of salicylic acid and 0.5 gram of sodium acetate. Add ammonia dropwise until the color changes from purple to brown. If the color is intense, dilute with water. Restore the purple color of the salicylate complex with a few drops of 1 : 1 hydrochloric acid, adding just enough to give a maximum color intensity. Titrate with EDTA solution. The titrating solution used for calcium and magnesium will serve if a microburet is used. With an ordinary buret a more dilute EDTA solution is necessary. The titer of the solution may be calculated from its CaO value, but it is best to standardize against a standard iron solution.

Manganese.—Add 5 ml of nitric acid and evaporate the aliquot taken for manganese to dryness on the steam bath. Repeat the evaporation with 2 ml of nitric acid to remove all chloride. Add 5 ml of nitric acid, 25 ml of water, and about 0.1 gram of potassium periodate. Boil until color develops, and keep hot for 2–3

hours. Cool, stand overnight, add 1 ml of phosphoric acid, transfer to a 50 ml volumetric flask, dilute to the mark and mix. Determine MnO_4^- photometrically.

Sulfur.—Dilute the filtrate from the ammonia precipitate (M_2O_3 group) to 100 ml and take aliquots as follows:

1. 50 ml for SO_3 (250 ml beaker)
2. 20 ml for CaO (200–250 ml conical flask)
3. 20 ml for MgO (200–250 ml conical flask).

To the 50 ml aliquot add 0.5 ml of 1:1 hydrochloric acid and heat to boiling. Add single drops of 10 percent barium chloride solution at 2–3 minute intervals until the sulfate is precipitated. Add 2 ml excess of barium chloride solution and digest hot for 2–3 hours. Cool and stand overnight. Stir in a little paper pulp and filter through a small S & S blue ribbon or a Whatman No. 42 paper. Wash with cold 1 percent hydrochloric acid. Ignite and weigh $BaSO_4$.

Calcium.—Prepare the following reagents:

EDTA solution.—Dissolve 29.5 grams of ethylenediamine tetraacetic acid and 8.3 grams of carbonate-free sodium hydroxide in water. Filter and dilute to 1 liter. Standardize against standard calcium solution.

Standard calcium solution.—Add 200–300 ml of water to 10 grams of pure dried $CaCO_3$ and dissolve with a slight excess of 1:1 hydrochloric acid, boil to remove carbon dioxide, cool, and dilute to 1 liter.

Alkaline cyanide.—Dissolve 40 grams of carbonate-free NaOH and 10 grams of potassium cyanide in 500 ml of water. Store in a polyethylene bottle.

Calcein indicator.—Grind together 0.25 gram of calcein, 2.5 grams of charcoal, and 25 grams of potassium chloride until the whole passes through a 115 mesh screen.

Eriochrome Black T.—Grind 0.25 gram of the indicator with 25 grams of potassium chloride.

Calcium may be determined either on the 10/100 aliquot of the filtrate from the insoluble material or on the 20/100 aliquot of the filtrate from the ammonia precipitate. Iron tends to obscure the end point in the first case, but satisfactory results are possible when Fe_2O_3 is less than about 2 percent, and a preliminary figure is usually obtainable. To the 10 ml aliquot add a little water, 0.05 gram of hydroxylamine hydrochloride, 5 ml of alkaline cyanide, and a small quantity of the calcein indicator. Titrate with EDTA solution using a 10 ml microburet graduated to 0.02 ml, and observing the color change against a white background in daylight. In the 20 ml aliquot, the procedure is the same, except that not more than 5–10 ml of water should be added before titration, and 10 ml of alkaline cyanide solution is used instead of 5. The smallest possible quantity of the indicator should be used, and some experimentation may be necessary by the analyst. Calcein imparts a green fluorescence to the solution, which must be ignored; the color change is from yellow to pink and is best observed by looking through the solution at a well-lighted white background.

In the titration of calcium, the volume of the solution must be controlled, especially when ammonium chloride is present, as in the 20 ml aliquot from the ammonia group filtrate. It is for this reason that a microburet and a relatively strong EDTA solution is used. With samples very high in MgO, dilution may be necessary to prevent interference by this element, and it is then necessary to add more alkali. A convenient indicator in such cases is brilliant cresyl blue. When a small piece of this indicator paper is dropped into the solution, it should turn pink at once, both before and after the titration. If it does not, insufficient alkali is present.

Magnesium.—If the minimum amount of calcein was used in the calcium titration on the 20 ml aliquot, magnesium may be determined directly on this solution after addition of ammonium chloride as follows.

Add to the solution at the calcium end point 10 ml of NH_4Cl solution (150 g/l), and enough Eriochrome Black T to give a strong pink color. Titrate slowly

until the color changes permanently to a pure blue. Because of the calcein present this end point is a little difficult, but the titration gives a good approximation to the volume of titrant which will be required for the CaO + MgO titration to be described, enabling a more rapid final titration.

Calcium + Magnesium.—Add to the 20 ml aliquot reserved for the purpose 0.05 g of hydroxylamine hydrochloride, 5 ml of NH_4Cl (150 g/l), 5 ml of alkaline cyanide, and enough Eriochrome Black T to give a good pink color. It is advisable to prepare a blank solution containing all the reagents and the indicator for use as a reference end point. Titrate with the same solution as was used for the calcium to a pure blue color.

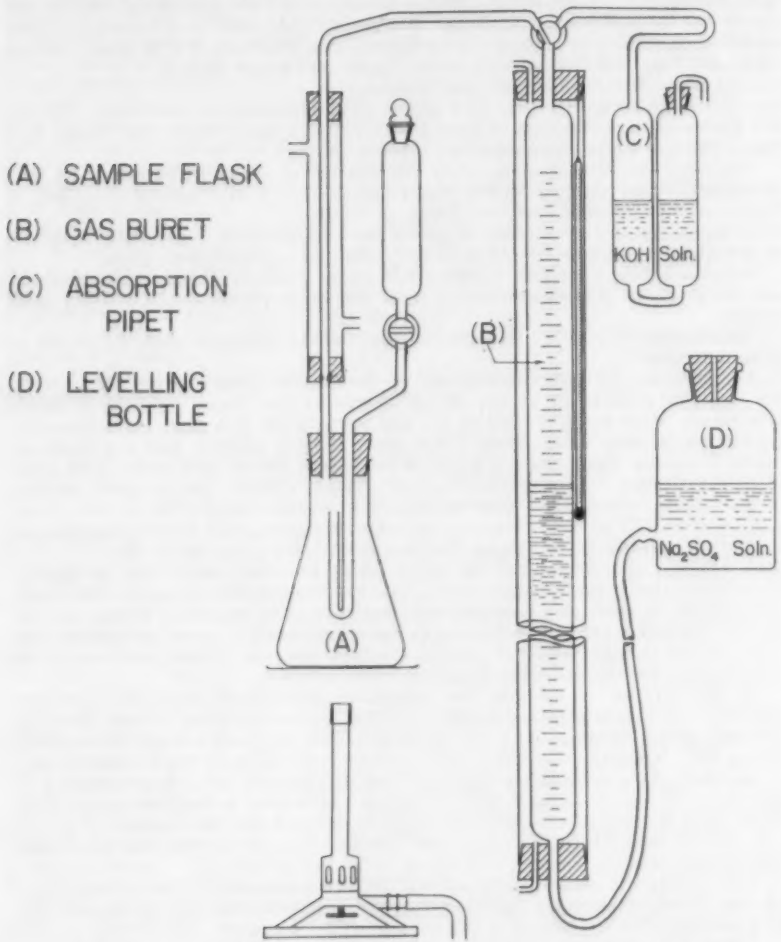

FIG. 1. Apparatus for gasometric determination of carbon dioxide.

Carbon Dioxide.—The apparatus (Fig. 1) for determination of carbon dioxide is a modification of that of Lunge and Rittener briefly described by Treadwell and Hall (7) and is similar to the apparatus of W. Geilmann (5). It consists essentially of a reaction flask with addition funnel, connected through a small return-flow condenser to a water-jacketed gas-measuring buret. The three-way stopcock on the buret may be opened either to the reaction flask or to an absorption pipet containing 40 percent potassium hydroxide solution. The containing fluid is a 20 percent sodium sulfate solution acidified with 1 percent of sulfuric acid and containing a little methyl orange. The procedure follows:

Transfer 0.15 to 0.3 gram of marl together with 1–2 grams of sodium chloride and a small piece of pure aluminum to the reaction flask, washing the sample from the weighing dish with CO_2-free water. By manipulating the levelling bottle and the stopcock, remove air from the absorption pipet and the buret, and fill the tube leading to the condenser with the Na_2SO_4 solution. Attach the flask containing the sample to the apparatus, and clamp it in place. Open the buret stopcock to the flask. Add about 10 ml of concentrated hydrochloric acid to the addition funnel, and run 5 ml or more of it into the flask. Heat to boiling, and boil gently for 30 minutes. The addition of aluminum and salt is necessary to remove completely CO_2 from the solution.

When reaction is complete, add about 35 ml of CO_2-free water to the addition funnel, lower the levelling bottle, and run the water into the flask until all the gases in the apparatus are transferred to the buret; then close the buret stopcock. Leave the stopcock on the addition funnel open. After about 5 minutes for temperature equilibrium to be reached, raise the levelling bottle until the liquid level in the buret coincides with that in the bottle, and read the buret, the thermometer suspended in the water jacket, and the barometer.

After the total volume of gases has been determined, open the stopcock to the absorption pipet, and raise the levelling bottle until the gases are transferred to the pipet. Allow 5 minutes for absorption of CO_2 to take place, and return the remaining gases (air, water vapor, hydrogen) to the buret. Again read the volume. The absorption process should be repeated once or more until a constant reading is obtained. The loss in volume is CO_2 absorbed.

To calculate the percent of carbon dioxide, the following expression is used:

$$\text{Percent } CO_2 = \frac{\text{volume difference (in ml)}}{22{,}414} \times \frac{273.2}{273.2 + t} \times \frac{\text{corrected pressure}}{760} \times \frac{44 \times 100}{\text{sample wt.}}$$

where t is the temperature in °C, and pressure is in mm of Hg.

The corrected pressure is obtained by converting the barometer reading to mm, and subtracting the vapor pressure of the sodium sulfate solution at the temperature of measurement.

An empirical method for quickly determining the vapor pressure correction was worked out on the basis of figures from "International Critical Tables," as follows:

t (°C)	Correction (mm)
27	$t - 6.0$
26	$t - 6.1$
25	$t - 6.2$
24	$t - 6.2$
23	$t - 6.2$

For example, if the temperature is 26.3° C, the vapor pressure correction is $26.3 - 6.1 = 20.2$ mm.

Certain precautions must be observed in making the CO_2 determination. It is necessary to add to the reaction flask before connecting it to the apparatus just enough water so that boiling may be carried out freely without the volume of air being so large that the buret capacity will be exceeded. A few trials may be necessary to determine the proper volume to use. In passing the gases from the absorption pipet to the buret prior to the final measurement, the meniscus must be allowed to drop slowly, at about the rate that an analytical buret drains. If the rate of transfer is too high, liquid will remain on the buret walls, giving too high a reading and a low value for CO_2. A blank run, using only CO_2-free water, salt, and a chip of aluminum, should be made frequently. This will always give a small positive result, even when no CO_2 is present, presumably because the sodium sulfate solution gives up a little dissolved CO_2. This difficulty will be particularly noticeable if temperature variations are large.

The buret should be thoroughly cleaned, so that the solution wets it completely. If Tygon tubing is used to connect it to the levelling bottle, chromic acid cleaning solution may be used to advantage without dismantling the apparatus. The buret stopcock should be cleaned and greased frequently to be sure that it is absolutely gas tight. If room temperature is not constant, water from a constant temperature bath may be kept circulating through the water jacket. Alternatively, air may be blown through the water in the jacket to mix it, in case a temperature gradient exists just before making the reading.

DISCUSSION OF RESULTS

Insoluble Material and SiO_2

The insoluble material reported in the rapid analyses is largely silica (Table 3), and generally the percentage is somewhat greater than that of SiO_2 because of the silicates that are attacked only partially or not at all during the acid evaporation. Two regular silicate analyses (Table 4) show that on the average the insoluble material is composed of more than 90 per cent SiO_2. Sample 10 (Table 4) is a composite of the insoluble residues from 13 marl samples from Warner and Fuller lakes in Stearns County, and Sample 11 is a composite of the residues from 18 samples from Nisswa Lake in Crow Wing County. Calculations similar to normative calculations for igneous rocks indicate that the residues contain approximately 8 percent of K-feldspar and 10

TABLE 4

ANALYSES OF INSOLUBLE RESIDUES FROM MARL SAMPLES
(Conventional Silicate Analyses)

	10	11		10	11
SiO_2	90.51	91.54	CaO	.95	.95
Al_2O_3	3.83	3.44	Na_2O	1.03	1.00
TiO_2	.29	.25	K_2O	1.31	1.11
Fe_2O_3	.99	.33	H_2O^-	.28	.33
FeO	.10	.20	Ignition loss	.41	.41
MnO	.01	.01			
MgO	.24	.21		99.95	99.78

10. Composite of insoluble residues from 13 samples from Warner and Fuller Lakes, Stearns County.

11. Composite of insoluble residues from 18 samples from Nisswa Lake, Crow Wing County. See analysis 5, Table 1 for bulk composition of marl.

per cent of silicic plagioclase. Close to 80 percent of the samples is silica in the form of detrital quartz or diatom tests.

The determination of SiO_2 by treatment of the siliceous residues with sulfuric and hydrofluoric acids, as has been suggested (1) in the analysis of limestone, is not recommended. The alkali metals and the alkaline earths in the residues are converted to sulfates, and the results for SiO_2 are apt to be erroneous as can be seen in the following data:

Sample No.	7 (F-5)	8 (F-34)
Insoluble material [1]	15.52	14.09
SiO_2 by HF treatment of insoluble material	13.56	12.44
SiO_2 [2]	14.40	13.34

[1] From Table 2, rapid analyses.
[2] From Table 1, conventional analyses.

In the rapid method the preliminary ignition of the samples renders some of the silicate minerals soluble in acid. If the ignition is omitted a larger percentage results for the insoluble material, because the silicates are largely unattacked. Samples 7 and 8, for example, by direct solution in acid followed by evaporation, gave 15.90 and 14.47 percent of insoluble material, respectively.

M_2O_3 and Al_2O_3

In the usual silicate analysis, Al_2O_3 is weighed together with the other oxides resulting from the ammonia precipitation, TiO_2, P_2O_5, and Fe_2O_3. These last are determined, and alumina is found by difference, because there is no satisfactory way of determining it directly. Failure to determine any of the other oxides will result in a high value for alumina.

In the analysis of the marl samples by the rapid method, the titanium and phosphorus contents of the ammonia precipitate are not determined. Some of the alumina and iron also remains in the insoluble residue in silicate minerals that are unattacked during the digestion with hydrochloric acid. As a result, the values for M_2O_3 differ from those for Al_2O_3 found by the regular procedure. Neglect of the TiO_2 and P_2O_5, and the retention of iron in the insoluble residue, make the M_2O_3 too high, and retention of alumina in the insolubles makes it too low.

The values reported as M_2O_3 in the rapid analyses are compared with those for alumina in Table 3.

Total Iron

Determinations of Fe_2O_3 by EDTA titration and with potassium dichromate are compared in Table 5. The EDTA titration compares favorably with the dichromate method, but results are generally lower in the rapid analyses because of the incomplete decomposition, some of the iron remaining with the insoluble residue.

TABLE 5

Fe_2O_3, CaO, AND MgO BY RAPID AND CONVENTIONAL METHODS

Sample	Fe_2O_3		CaO		MgO	
	Rapid	Conventional	Rapid	Conventional	Rapid	Conventional
1	0.24 .25	0.24	51.69	51.61	1.23	1.23
2	.70	.73	49.05	49.13 49.08	1.50	1.50
3	.41 .42	.44	47.36 47.36	47.36	1.49	1.32
4	.30	.35	42.39 42.43*	42.39	1.47	1.45
5	.78	.82	42.41	42.34	1.05	1.11
6	.64 .64	.71	41.62 41.57 41.57 41.45*	41.56	1.56 1.53	1.54
7	1.02	1.14	39.97 39.89 39.67*	39.96	1.85	1.81
8	1.43 1.42	1.52	39.54 39.47 39.43*	39.56	1.41	1.40
9	2.21 2.22	2.43	30.75 30.72	30.82	1.70 1.71	1.79

* Determination made directly on sample dissolved in acid without preliminary separations.

Calcium and Magnesium

The EDTA method for CaO and MgO compares favorably with the gravimetric technique (Table 5). With magnesium, great care is necessary during the titration if accurate results are required, particularly when magnesium is low. This is largely because MgO is not determined directly but as the difference between determinations of CaO and of CaO + MgO. The following data for three samples of dolomitic limestone show that the method may be used for materials high in magnesium:

Sample	CaO		MgO	
	Rapid	Regular	Rapid	Regular
A	30.42	30.72	18.95	19.18
B	29.00	29.14	14.15	14.27
C	38.73	38.97	8.52	8.61

Volatile Constituents

The volatile constituents of the marl samples that are lost on ignition at high temperature include water, carbon dioxide, sulfur, and organic matter. The weight loss depends on the heating conditions. The figures reported as ignition in Tables 1 and 2 are the total loss on ignition minus the values found for H_2O- and CO_2; ignition is then a measure of the organic matter and the H_2O+ contents of the samples.

Loss on Ignition.—Comparative figures for loss on ignition in the rapid and refined analyses are given in Table 6. Duplicate determinations on samples 2 and 6 in the rapid analyses show good reproducibility when the samples are ignited in porcelain crucibles in the muffle furnace. In the regular analyses the samples were ignited in platinum crucibles over Tirrill and Meker burners. Ignition periods of 6–8 hours over the Tirrill burner were required to completely destroy the organic material, and an additional 6–8 hours over the Meker burner were required to bring the sample to constant weight. Ignition in platinum crucibles tends to cause some loss of sulfur, and this loss gives a higher result for loss on ignition. In Sample 8, for example, only 0.03 percent of sulfur as SO_3 was found in the residue after ignition in a platinum crucible, although the SO_3 content of the original sample is 0.70 percent. The loss on ignition for this sample in platinum is 41.01 percent compared to 40.27 percent in porcelain.

Water.—It is customary in silicate analysis to report the loss of water, commonly termed moisture, at a temperature below 110° C as H_2O- and

TABLE 6

H_2O- AND LOSS ON IGNITION BY RAPID AND CONVENTIONAL METHODS

Sample	Total loss on ignition		H_2O-		Ignition*	
	Rapid	Conventional	Rapid	Conventional	Rapid	Conventional
1	45.59	45.61 M	.57	.54	3.19	3.41
2	44.31 44.35	44.47 T	.70 .60	.73	3.91 4.05	3.81
3	43.71	43.72 M	1.06	1.11	4.38	4.38
4	44.18	44.18 M	1.62	1.62	7.99	8.06
5	44.91	44.92 T	1.57	1.52	9.65	9.70
6	45.29 45.30 45.25	45.29 M	1.68 1.52 1.54	1.68	10.17 10.34 10.27	9.95
7	39.24	39.15 M	1.14	1.09	5.56	5.42
8	40.27	41.01 M	1.48	1.48	6.91	7.23
9	43.80	43.96 T	2.62	2.78	16.13	16.18

M—Meker burner, T—Tirrill burner. * Total loss on ignition minus CO_2 and H_2O-.

the loss above 110° C as H_2O+. In practice the total H_2O content is determined, and the loss of weight on drying at 110° C (H_2O-) is subtracted to arrive at the figure for H_2O+. The large amount of organic matter in the marl samples makes the determination of total water difficult, and attempts in the present study were unsatisfactory.

Moisture.—H_2O- is determined by drying a 1-gram sample in an electric oven. Drying periods of 1 to 2 hours were unsatisfactory and gave widely varying results. In part this may be caused by adsorbed water which is held tightly by finely divided particles, and in part by the organic matter in the marl. Comparative results are given in Table 6.

Carbon Dioxide.—Comparative results (Table 7) show that the gasometric method used in the rapid analysis compares favorably with the conventional gravimetric method for the determination of carbon dioxide. The gravimetric method involves evolution of the CO_2 by dissolving the sample in acid. The gas is trapped in an ascarite absorption tube and weighed. The large amounts of CO_2 in the samples require frequent replacement of the ascarite, and for this reason the gasometric method is preferred.

Sulfur.—The form of the sulfur in the marl is not entirely known, and it is likely that it is present in a number of compounds. An extraction test by H. Roepke shows that a small part of the sulfur is in elemental form and can be extracted with benzene. Some of the sulfur may be present in organic compounds, as finely divided sulfide, or as sulfate. In the absence of precise information on the state of oxidation of the sulfur, total sulfur is reported in all analyses as SO_3.

Ignition of the samples in the muffle furnace in the rapid analytical procedure converts the sulfur to sulfate and permits its determination in an aliquot of the first filtrate. Because some of the sulfur is lost during ignition of the sample in a platinum crucible, sulfur was determined in the regular analysis by treating a separate 1-gram sample with brominated hydrochloric acid. Figures for sulfur by both procedures are given in Table 7. The somewhat

TABLE 7

CO_2 AND SO_3 BY RAPID AND CONVENTIONAL METHODS

Sample	CO_2		SO_3	
	Gasometric	Gravimetric	Rapid	Conventional
1	41.83	41.66	0.60	n.d.
2	39.70	39.93	.57	.57
3	38.27	38.23	.41	.40
4	34.57	34.50	.77	.73
5	33.69	33.70	1.13	n.d.
6	33.44	33.66	.49 .47	.44
7	32.54	32.64	.99	.97
8	31.88	32.30	.69 .70	.62
9	25.05	25.00	.76	.74

higher values and reproducibility of figures in the rapid method suggests that this is the better procedure.

Ignition.—The figures reported as ignition in Tables 1 and 2, the difference between the total loss on ignition and the figures for CO_2 plus H_2O-, include organic matter and the water remaining in the sample after drying at 110° C. A comparison of the values obtained by the two analytical procedures (Table 6) shows some rather large differences. In part these are caused by differences in the determinations of CO_2, H_2O-, and total loss on ignition. Values for ignition range from 3 to 16 percent in the analyzed samples, and in large part these figures represent the organic matter content of the samples.

Total carbon as CO_2 was determined in Sample 3 using a combustion train designed for the determination of carbon in rocks. Total CO_2 in the sample was found to be 44.75 percent; carbonate CO_2 (Table 1) in this sample is 38.23 percent; and the difference of 6.52 percent can be assigned to CO_2 from the burning of carbon of the organic matter. If a composition of CH_2O is assumed for the organic matter, 4.45 percent by weight is calculated for the content of organic matter in the sample compared to 4.38 percent reported as ignition.

CONCLUDING REMARKS

The Minnesota lake marl is a mixture of complex origin, the result of chemical, organic, and physical processes. The principal component is calcium carbonate brought to the lakes by streams and ground water and precipitated biochemically; however, some of the carbonate is the accumulation of shells of ostracodes, pelecypods, and gastropods that live in the lake water. Clastic material carried into the lakes by streams include quartz, feldspar and minor amounts of clay minerals and other silicates. The clastic component contributes to the silica content, but in part the silica is the result of organic processes and represents the accumulation of tests of fresh-water diatoms. A large amount of organic material is present, and in the late stage of development of the lake deposits there is a transition from marl accumulation to peat bog development.

The organic matter complicates the analysis and precludes determination of ferrous iron and of total water. Ignition of the sample to destroy the organic matter is prerequisite to a good analysis, and the ignition of the marl in a porcelain crucible in a muffle furnace is a preferred technique, superior to ignition in platinum crucibles over open gas burners.

Ignition of the samples renders some of the silicates soluble in hydrochloric acid, and evaporation to dryness to dehydrate the silica is necessary; however, not all the silicate minerals are soluble, and the insoluble material contains silicates as well as silica. Treatment of the insoluble material with hydrofluoric acid to volatilize the silica is an unreliable procedure and is not recommended. The incomplete attack of the silicates minerals makes determination of Al_2O_3 impossible, because some of the alumina remains with the insoluble material. Titanium, phosphorus, and, to some extent, iron

likewise are divided between the insoluble material and the ammonia group. The rapid analysis, therefore, is not strictly comparable to the conventional analysis, and the geologist will do well to keep in mind the salient differences.

The rapid method used in the marl analyses has a great advantage over the conventional procedure in that, as implied in the name, the time for an analysis is greatly reduced. Over 80 samples of Minnesota lake marl have been analyzed, and the results will be published by the Minnesota State Iron Range Resources and Rehabilitation Commission. The analytical procedures outlined in this paper with or without modification can be applied to the study of many limestones, dolomites, and other carbonate materials. Good precision in the determinations of CaO, MgO, and CO_2 is obtainable, but as is true of any analytical procedure, proper care and some chemical sense are required in the execution of the analysis to obtain the maximum benefit.

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A COMPARISON BETWEEN THE COMMON LEAD ISOTOPIC COMPOSITION AND MINOR BASE METAL CONTENTS OF SOME FINNISH GALENAS

O. VAASJOKI AND OLAVI KOUVO

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ABSTRACT

In this article the authors present the results obtained by a geochemical investigation of some Finnish galenas. The spectrographic and mass spectrographic data show that two groups of galenas may be distinguished on the basis of minor base metal contents and lead isotope compositions. The significance of the differences observed is discussed, and the bearing on the source material and deposition of the ore occurrences is given.

INTRODUCTION

THE basement rocks of Southern Finland have inspired a number of special investigations, some of which are of classic significance in the domain of Precambrian geology. In these investigations the study of stratigraphic relations has been one of the main topics—a problem that is linked with the stratigraphic investigations of the whole country. A basis for this kind of study as well as a coordinative schema of the stratigraphy in Finland was established by Sederholm (5) and the work has been continued by several other investigators, especially by Väyrynen (11) and Simonen (6). According to the conception generally accepted, it seems that the Archean basement rocks of Finland have been produced and influenced by two orogenic cycles. These are called Svecofennian and Karelian orogenies. The formations belonging to the Svecofennian province trend approximately from west to east in Southern and Western Finland, whereas the formations belonging to the Karelian orogeny run approximately from SE to NW in the eastern and northern parts of the country. In this connection it is of importance to know that the granodioritic gneissic granites of Southern Finland have been considered representatives of the series of intrusives belonging to the synkinematic phase of the Svecofennian orogeny. Similarly it is a general belief that the rapakivi repre-

sents formations belonging to the postkinematic, i.e., to the last phase of the Karelian orogeny. The correlation between the supposed orogenic cycles and the corresponding series of intrusives, represented by different types of granites has, of course, been the subject of many divergent discussions among Finnish geologists. This is especially so, because there has not been a sufficient number of absolute age determinations available so far.

As regards the base metal deposits in the Svecofennian province, it has been suggested that the occurrences of complex sulfide ores firstly belong genetically to the formations of the synkinematic phase or as expressed in everyday language: "The synkinematic gneissic granites (oligoclase granites) have been the ore-bearers." This opinion has its primary basis in the results of the Orijärvi investigation by Eskola (3) which sets forth the idea that the sulfide ores in the region have been formed as a result of metasomatic processes in connection with the intrusive activity in the synkinematic phase of the Svecofennian orogeny. There are, however, within the Svecofennian province some examples of occurrences for which some other interpretation than the one given above seems to be more justified. An example of this is the ore mineralizations in Koskenkylä, Pernaja district, where the first author arrived at the

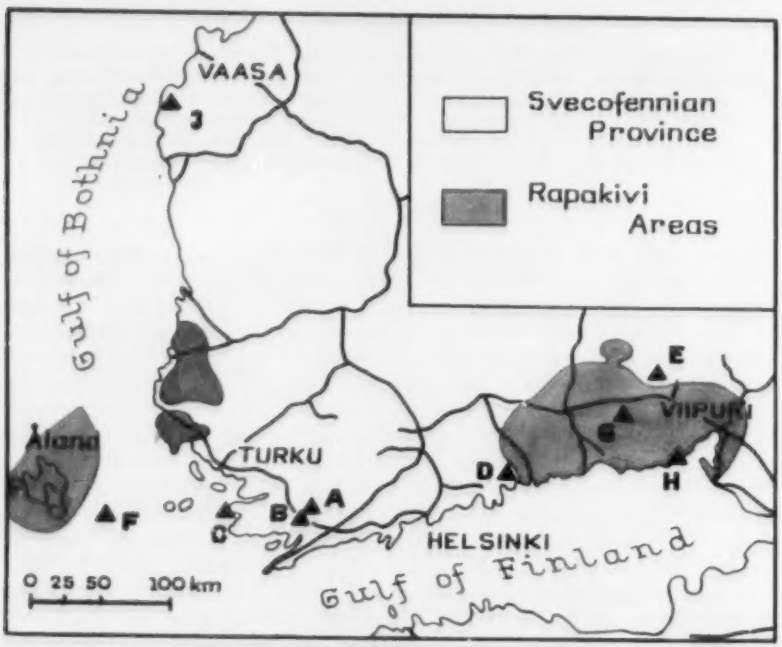

FIG. 1. Schematic map showing the locations of samples studied and the principal areas of the rapakivi. The area assigned as Svecofennian province includes minor amounts of younger formations.

conclusion that the emplacement of the ore into the present environment took place in the late-kinematic phase. The possibility must be borne in mind in this case, however, that the material for ore mineralization may be a product of remobilization of a material originally concentrated in an earlier phase of the Svecofennian orogeny (8). The ore mineralization of this area is situated at a distance of only 2 km from the border of the vast rapakivi massif of Viipuri. Therefore, there still exists the possibility that the ore mineralization in Koskenkylä area has been caused by the hydrothermal activity connected with the intrusion of rapakivi magmas.

In this study the authors have tried firstly to estimate which phase of the orogeny might have been responsible for producing the variety of sulfide ores found in the Svecofennian province. Secondly, the question of whether some of the ores of Southern Finland have been formed during the Svecofennian cycle or at a later date, has been taken into consideration. In each of these questions the minor base metal content and the lead isotope composition of the galenas have been used as criteria.

The minor base metal content of the galenas separated from selected sulfide ore specimens from the occurrences of Southern Finland, have been investigated earlier by the first author (9). The essential results of this study may be referred to in this connection. Most of the facts included in the paper at hand were tentatively discussed at the III Winter Session of Scandinavian Geologists, January 1958 in Helsinki (10). Since then galena from Korsnäs has been added to the material investigated.

OCCURRENCES INVESTIGATED, THEIR ORE MINERAL ASSOCIATIONS AND MINOR BASE METAL CONTENTS OF THE GALENAS

The material under investigation has been collected from the localities shown in Figure 1. Considering the stratigraphical position of the corresponding occurrences, the specimens have been selected as follows:

A. Orijärvi Mine, Kisko B. Aijala Mine, Kisko C. Attu, Parainen I. Korsnäs	Occurrences from the Svecofennian province
G. Luotola, Luumäki H. Lamminniemi, Säkkijärvi	Occurrences from the rapakivi areas
D. Koskenkylä, Pernaja E. Hyvärilä, Lemi F. Södö, Sottunga	Occurrences from the Svecofennian province close to the borders of rapakivi massifs

It is common observation that there are many different ore minerals in the galena-bearing ores from the Svecofennian zone. Usual minerals are: chalcopyrite, pyrite, pyrrhotite, marcasite, galena, sphalerite, arsenopyrite, and/or löllingite, and in places magnetite. Galena is commonly associated with Sb—Bi—sulfo minerals such as tetrahedrite, jamesonite, boulangerite,

TABLE 1

THE MAIN ORE MINERAL COMPOSITION OF THE OCCURRENCES STUDIED

Ore mineral	A. Orijärvi	B. Aijala	C. Attu	D. Koskenkylä	I. Korsnäs	E. Hyvärilä	F. Södö	G. Luotola	H. Lamminniemi
Sphalerite	x	x	x	x		x			
Pyrrhotite	x	x	x	x	x	x			
Arsenopyrite		x		x					
Sulfo minerals	x	x	x	x					
Pyrite	x	x	x	x	x		x		
Galena	x	x	x	x	x	x	x	x	x
Chalcopyrite	x	x	x	x	x	x	x	x	x
Chalcosite								x	x
Covellite							x	x	x

cosalite, selenocosalite, meneghenite, guanajuatite etc. It should be mentioned that in connection with the galena from Korsnäs no sulfo minerals have been observed so far.

The ore mineral association connected with the rapakivi occurrences seems on the contrary to be more simple. Galena is the main ore mineral, accompanied by small amounts of the replacement series chalcopyrite, chalcocite and covellite. The sulfo minerals have not been observed.

The principal ore mineral associations in the specimens studied from the

TABLE 2

THE DISTRIBUTION OF MINOR BASE METALS IN THE GALENAS

Locality	Element in ppm						
	Ag	Sb	Bi	Sn	Cd	As	Zn
A Orijärvi Mine	1,000	60	4,000	50	+	+	–
B Aijala Mine	800	1,000	900	80	150	+	–[1]
I Korsnäs	62	50	4,600	10	300[2]	100[2]	10[2]
C Attu	200	1,200	90	150	+	+	–
D Koskenkylä	600	120	200	5	+	1,000[2]	–
E Hyvärilä	1,000	60	high	high	+	+	–
F Södö	30	+	4	+	+	+	–
G Luotola	20	+	2	+	+	+	–
H Lamminniemi	15	60	2	+	+	+	–
		+ >60	high = over 4,000	+ <3	+ <100	+ <100	

[1] Very low.
[2] Probably caused by impurity.

different localities are summarized in Table 1, mainly according to the results obtained by the first author in his earlier study (9).

As observed from Table 1, in the occurrences of Koskenkylä (D) and Hyvärilä (E) the ore mineral associations are typically those found in the occurrences of the Svecofennian zone. On the other hand, the ore mineral association of the occurrence at Södö is equivalent to that which has been identified from the occurrences of the rapakivi areas. After separation of the galenas from the different specimens, the fractions obtained have been spectrographically analyzed with regard to the minor base metal contents. The results of these analyses are shown in Table 2.

COMMON LEAD ISOTOPE ABUNDANCES AND S^{32}/S^{34} RATIOS

The isotope analyses and computation of the lead ages were carried out by the second author while working in 1956–57 at the Lamont Geological Observatory, Columbia University, New York. The computations are based on the methods applied at this institute (2). The isotopic composition of the lead, the lead ages and the sulfur isotope ratios of the galenas studied are shown in Table 3.

TABLE 3

THE LEAD ISOTOPE COMPOSITIONS AND SULFUR ISOTOPE RATIOS

Locality	Lead isotope compositions			Age (m.y.)	Sulfur isotope ratios[1]	
	$\frac{206}{204}$	$\frac{207}{204}$	$\frac{208}{204}$		$\frac{S\ 32}{S\ 34}$	$\frac{S\ 34}{0/00}$
A Orijärvi Mine	15.80	15.46	35.88	1,770	22.21	+0.0
B Aijala Mine	15.95	15.64	36.24	1,820	22.27	−2.7
I Korsnäs	15.95	15.57	36.26	1,772	22.26	−2.3
C Attu	15.82	15.47	35.89	1,770	22.22	−0.5
D Koskenkylä	15.85	15.51	36.00	1,790	22.14	+3.2
E Hyvärilä	16.13	15.60	36.42	1,650	21.94	+12.2
F Södö	22.30	16.42	40.54	+	22.52	−14.0
G Luotola	19.33	16.31	39.61	170	21.43	+35.1
H Lamminniemi	19.15	15.80	39.13	+	21.60	+27.5

[1] Ault (1957).

CORRELATION OF THE RESULTS

In the following pages a correlation of the results obtained by the different determinations will be made, as well as a correlation of these results to the two main topics of the present paper. The minor base metal contents in the galenas A, B, C, D, E, and I are analogous. There are practically no minor base metals in the galenas F, G, and H, and the lead isotope composition of these galenas is also very similar. As regards both these properties, however, the group of galenas F, G, and H deviate sharply from the former group of galenas.

Although in this paper no further attention will be paid to the sulfur isotope composition of the galenas investigated (1), it is worth while, however, on

the basis of the S^{32}/S^{34} ratios, to point out the following characteristic features (7):

1. The isotopic composition of sulfur in the galenas A, B, C, D, and I approximates sulfur of meteoric composition.

2. The isotopic composition of sulfur in the galenas E, G, and H is close to the isotopic composition of sulfur as determined for sulfur in the ocean water.

3. The isotopic composition of sulfur in the galenas from Södö (F) resembles the composition of sulfur typical for materials of biogenic origin.

In the light of the isotopic constitution of the leads, it is obvious that the galenas A, B, C, D, E, and I belong to one group. By means of micas and zircons the second author has determined the age of Svecofennian synkinematic intrusives to be 1,790 m.y. and by the same means he has determined the age of rapakivi rocks to be 1,620 m.y. (4). The magnitude of these ages is in accordance with the recent determinations made by other investigators concerning the same group of rocks. The ages of the galenas A, B, C, D, E, and I are very close to the ages of their host rocks, which are considered to represent the synkinematic Svecofennian intrusive rocks. It therefore seems as if the results obtained may justify the earlier opinion that the genesis of the sulfide ore deposits of Southern Finland including these galenas was closely related to the processes producing the Svecofennian formations synkinematic in character (3).

The galenas F, G, and H appear as one coherent group not only with regard to the minor base metal contents, but also with reference to the lead isotope compositions. The ages computed for these galenas appear to be anomalous as regards the lead isotope compositions. This is obviously in accordance with field evidence, which reveals that all of the galenas F, G, and H occur in younger fissure fillings, and thus the mineralizations as related to their rapakivi host are undoubtedly epigenetic in character (9).

Presuming that the lead in all the galenas here investigated, was from a common source, it follows that after the emplacement of the galenas A, B, C, D, E, and I the material for the galenas F, G, and H has been contaminated by additional radiogenic lead later on. Similar assumptions are valid, even if the material for galenas F, G, and H was a product of a rejuvenated material originally emplaced in the Svecofennian cycle. Thus, the hypothesis of a common source material for the galenas of the Svecofennian and rapakivi groups obviously encounters complexity of interpretation. This complexity of interpretation based on the isotopic constitution of the leads in the galenas investigated, however, may be disregarded if attention is given to the results obtained by the analyses of minor base metals. Apparently the fact that the minor base metal contents in the galenas of the Svecofennian group vs. those in the galenas of the rapakivi group supports the opinion that there is a different source material in each of these galena groups.

CONCLUSIONS

After estimation of the results obtained the following conclusions may be drawn as regards the material studied:

1. In the occurrences situated within the Svecofennian province in Southern Finland the galenas seem to be of a similar age. These ages are comparable to the ages of the intrusives supposed to be synkinematic in character as related to the Svecofennian orogenic cycle. This circumstance further supports the idea that the ore mineralizations concerned, in accordance with the earlier opinion, may be considered syngenetic in relation to the synkinematic phase of the orogeny. If the ore material of these mineralizations in a later stage of the orogeny has been remobilized and has migrated to a new environment, the isotopic constitution of lead probably has not changed. This may be proved by the isotopic constitution of lead in the galena from the occurrence in Koskenkylä, which is supposed to have been emplaced in the late kinematic phase of the Svecofennian orogeny (8).

2. In the ore minerals that occur in the rapakivi areas the ages of the galenas are very young or anomalous. According to the field evidence these ores occur as fissure fillings and obviously are much younger than the rapakivi host.

3. In the ore minerals investigated from the rapakivi areas the original ore material as compared with the source material of the ore deposits of the Svecofennian province might have been of different composition.

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SCIENTIFIC COMMUNICATIONS

MOUNTING OF GEOLOGICAL SPECIMENS IN CLEAR, COLD SETTING PLASTIC

Present thermosetting mounting materials and equipment have always been inadequate due to the necessary time, temperature, and pressure involved, and the inescapable fact that a variety of molds of different shapes and sizes would be prohibitive in cost and time consuming to change when required.

These limitations brought about a search in this laboratory for a new and better way to mount metallographic specimens.

Because of the known properties of Epoxy resins, our effort was concentrated on this material with the following results:

To every 100 grams of Bakelite ERL2795 Epoxy Resin, add 10 grams of Hysol Cl hardener. Stir with a small electric food mixer in a 16 oz waxed paper cup for approximately one minute. Place tray of rubber molds with samples inside before a window air conditioner set at its coldest temperature. Pour epoxy into molds and let set for six-seven hours. Remove from air conditioner to warm molds to room temperature, peel back rubber mold and mount is then ready to grind and polish. Figure 1 shows some geological and other specimens mounted and polished using this method.

Two sizes of natural rubber cups are used in this laboratory. One is 1⅜″ I.D. and the other is 2¼″ I.D. They are made by Anchor Packing Company. Before pouring epoxy, these cups must be brushed with undiluted Spraylat PM4571. This is a mold release and can be easily washed off after each mount is removed. These cups have lasted us on the average of 200 mountings each. It is possible with this method for one man to mount 500 specimens in one day. This laboratory mounts approximately 15,000 metal specimens each year using our epoxy method. Of this total, 15 percent are over 1″ wide × 2″ long. Samples up to 4″ wide by 8″ long have been mounted successfully. For the larger sizes, hardener should be reduced to 9 grams per 100 grams epoxy and molds (Polyethylene containers with no Spraylat applied) should be set in a tray of water with the water level above that of the plastic. Installation of a timer on the air conditioner would allow pouring of plastic even a few minutes before quitting time. Identification of samples is retained by using different colored drops of Tech-Pen Ink on the back of each and then putting the same Ink dots on a piece of paper that contains each identification. All mounts are ready to grind and polish the day after they are poured. Any non-acrylic type lacquer can be used to make the back of the mount transparent after necessary grinding.

FIG. 1.

No temperature rise above 100° F occurs with this method, no applied pressure is involved, and the shrinkage is at a minimum. Adhesion to most all materials is excellent, even such polished objects as ball bearings. Complete sample is visible at all times and there are no seepage areas in the mount, since this material flows easily into all crevices and adheres tightly to the sample.

The General Electric Large Steam Turbine-Generator Department, Materials & Processes Laboratory Metallographic Group uses this method of mounting exclusively. Production of mounts for all samples received in one day in this laboratory could never be sustained using the old method of hydraulic presses and thermosetting plastics. By this method, we have given our engineers approximately fifteen times more surface area to examine than we normally could, using the same number of personnel.

Other metallographic specimens we have successfully mounted and polished by this method are ceramics, carbon brushes, graphite, coal and charcoal, hard and brittle resins, wood, low temperature solders and babbitts, extracted teeth, one mil wire for structure, graphite ores, and even small insects, experimentally, to determine the appearance of a polished cross section.

A complete report of this process can be had by writing to the author.

NORMAN J. GENDRON

GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.,
Dec. 13, 1958

THE APPLICATION OF WHITE SPIRIT IN FIELD DITHIZONE COLORIMETRY [1]

V. G. HILL

ABSTRACT

White spirit (mineral turpentine) has been investigated as a solvent in field dithizone colorimetry and found to be quite suitable. The difference in the solubility of the copper dithizonate from the lead and zinc dithizonates at a pH of 8.5 can be used to distinguish the presence of these metals.

During the past year the author has been engaged on a regional Geochemical Prospecting Survey for copper over an area of several thousand square miles in Central Ghana. From the outset of the program it was obvious that one of the problems would be the obtaining of adequate supplies of organic solvent to dissolve the dithizone. Because of the difficulties involved in importing large quantities of reagent grade chemicals like xylene and chloroform at short notice it was decided to resort to more unorthodox solvents, the most promising of which was white spirit [2] (mineral turpentine) introduced by Holman (2). The use of this solvent was investigated, tested and tried with surprising success during the past nine months. We have examined over 40,000 soil samples using it as the organic solvent, and it now appears to be superior to xylene and other lighter than water solvents, and is most ideally suitable for field dithizone colorimetry.

[1] Published by permission of the Director, Geological Survey Department, Ghana.

[2] White spirit (mineral turpentine) is a high boiling fraction in petroleum distillation. The product used was obtained from the Shell Company of West Africa Ltd. It is composed principally of aliphatic hydro carbons with 15 percent aromatic compounds. The S.G. at 60° C is 0.7788 and distillation range 150–194° C.

The use of white spirit necessitates only a minor modification in the cold citrate extraction method (1) and it can be used as the lighter than water solvent in all phases of field dithizone methods.

PURIFICATION

White spirit as obtained commercially is impure and has to be purified by successive extractions with 5 percent of its volume of concentrated sulfuric acid until the acid layer is almost colorless after shaking for twenty seconds. Considerable economy in acid consumption can be effected by re-using the acid and only using fresh supplies for the last two or three extractions. The amount of shaking can be significantly reduced if the white spirit is allowed to stand over the acid for some time. A batch method using seven winchester quarts for the preliminary extractions proved to be quite satisfactory. The extracted white spirit is neutralized with calcium carbonate A.R. and then filtered through Whatman's No. 4 or any other open filter paper. Distillation is not necessary.

DITHIZONE SOLUTIONS AND DITHIZONATES

Dithizone is only very slightly soluble in white spirit so it is necessary to prepare a strong solution of dithizone in chloroform or carbon-tetrachloride and then dilute it with white spirit when required. The greater solubility of dithizone in chloroform makes this solvent preferable in that the specific gravity of the white spirit is not significantly increased. A 0.200 percent dithizone solution in chloroform as used by Holman was found to be convenient. For field methods this solution is diluted to 0.0040 percent or any other convenient strength with white spirit. The necessary precautions for storage are to be observed (3, p. 108).

The dithizone solution diluted with white spirit is relatively stable if properly handled. A 0.008 percent solution shows little change when stored under the conditions indicated in columns 1 and 2 of Table 1. It should be noted that the decomposition proceeds very slowly at first, but gradually increases until at the end of the time given in column 3 all the dithizone is decomposed.

The absorption curves of dithizone, and the dithizonates of copper and lead in white spirit were determined over the range 375–850 mμ with a Bausch and Lomb "Spectronic 20" and are similar to those given by Sandell (3, p. 102) using other solvents. The copper dithizonate prepared at pH of 8.5 was only slightly soluble in the organic layer and separated out at the interface of the aqueous and organic layers as a brown scum. This is probably the enol form. If the reaction is done at a pH of 2.5 then the violet red color of the copper dithizonate is produced in the organic layer. The zinc dithi-

TABLE 1

STABILITY OF 0.0008 PERCENT DITHIZONE SOLUTION IN WHITE SPIRIT

Condition		Period of Stability	Interval of Decomposition
Diffused light	80° C	0.5 hour	6 hours
Dark	80° C	2.5 hours	8 days
Dark	40° C	4 days	> 14 days

zonate is easily formed at pH of 8.5. The colors of these metal dithizonates are relatively stable even when exposed to diffused light.

APPLICATION TO DITHIZONE COLORIMETRY

Our use of white spirit in dithizone colorimetry was almost entirely confined to field methods using a slightly modified cold citrate extraction method (1). The citrate solution after removal of the heavy metals by extraction with 0.01 percent dithizone in carbon tetrachloride, was brought to equilibrium with 0.004 percent dithizone solution in white spirit by shaking them together in a separatory funnel until two successive lots of the dithizone solution did not show any visible color change. The procedure given by Bloom (1) for total exchangeable heavy metals is then followed.

The difference in the solubilities in white spirit of the copper dithizonate as compared to the lead and zinc dithizonates at a pH of 8.5 may be used to advantage as a means of determining the metal causing the reaction. For example if the organic layer assumes a bright red color during the test then the principal heavy metal present is lead or zinc, or a mixture of these. It is not possible to distinguish these under the conditions of the experiment. However the addition of cyanide ion to the solution will depress the reaction of zinc but not lead. If the organic layer becomes colorless or bleached then copper is the principal heavy metal present. In practice however all three of these heavy metals may be present in varying amounts but the bleaching of the color of the dithizone layer may still be used as a safe guide in distinguishing these metals. Reference specimens of the various dithizonates may be helpful.

The white spirit dithizone solution may also be used in field methods requiring a preliminary acid digestion or fusion followed by acid extraction. In all cases the procedure is exactly the same as if xylene were the organic solvent. The stability of the white spirit dithizone solutions increases the precision of the test because the steady drift in the results during the course of the day due to the decomposition of the dithizone by solvents like xylene is negligible here.

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DISCUSSIONS

THE OCCURRENCE OF URANIUM IN ANCIENT CONGLOMERATES

Sir: Dr. Davidson's paper (vol. 52, p. 668–693) provokes comment when he states: (p. 678) "At the present time the placer theory is sustained almost solely by the monographs of Ramdhor (55) and Liebenberg or the mineragraphy of the Witwatersrand Ores." In fact, the data that support a placer origin rather than a hydrothermal come largely from a study of the mineral provinces, districts and epochs of the Transvaal and Southern Rhodesia. Whether it is a profound study of all the gold deposits in the Transvaal and Southern Rhodesia, as one mineral province, or whether the study is devoted to detailed geological sections of the Witwatersrand System, the result is the same—there is no evidence of any magmatic source for hydrothermal solutions to mineralize either the Witwatersrand Conglomerates or the Black Reef Conglomerates. This alone would not be very helpful but when any particular deposit is examined in detail, then the difficulty of accepting a hydrothermal origin is increased. It must be borne in mind that many South African geologists are familiar with important gold deposits that are of hydrothermal origin, generally associated with some nearby magmatic body that could have caused the mineralization. For example, Mendelssohn (16) speaking of the origin of the gold deposits of the Murchison Range states "The ore bodies discussed in this paper undoubtedly owe their origin to hydrothermal solutions resulting from the crystallization of a deep seated intrusive magma, probably of acid or acid intermediate composition."

Van Eeden et al. (21) speak of granitic matter permeating the whole of the schist belt, and there is reason therefore to accept such an hypothesis as reasonable for the evidence is very clear, even if it be solely circumstantial, but such evidence is lacking in the case of the Witwatersrand and it has been thoroughly explored in depth and the surface exposures are good. I have drawn a section through the Central Witwatersrand from the Bushveld Complex north of Pretoria to the Transvaal System to the South of Johannesburg in which the vertical scale is the same as the horizontal, namely 1 : 150,000 approximately. All the data that could be obtained from mining records have been shown distinctly from the geophysical data and extrapolations indicated. From this section it is difficult to see where hydrothermal solutions could arise from depth and solely mineralize the conglomerate bands in the Upper Division of the Witwatersrand System and not affect the shale-quartzite contacts in the Lower Division. Whatever feeding channels existed, must have been extremely numerous to mineralize many horizons of conglomerates over the vast extent of the Witwatersrand gold field. In some instances, for example,

the Bird Reef series on the West Rand, the gold-uranium ratios are different from those in the normal reef. These channels, if they existed, had to come up through the whole of the Lower Division of 15,000 feet in which as du Toit says: "Apart from the conversion of arenaceous types into quarzites by the deposition of secondary silica and the development of sericitic mica or chloritoid in the slaty types, there has been no extreme metamorphism. A conspicuous exception in the Parys area, where the strata exhibit intense alteration, due in part to a subjacent igneous body." These rocks could, purely from field data and not by inference from petrographic data, undergo metamorphism. The only evidence of a magmatic body within the Witwatersrand is the Marievale granophyre, a very local body on the eastern Witwatersrand. Indeed the evidence is that any magma that existed below the Witwatersrand system was of andesitic composition giving rise to the Ventersdorp lavas and later the Ongeluk lavas in the Pretoria series. Could such a magma or emanations from it have given rise to the gold, uranium and platenoids in the bankets? I suggest that this alone makes the hydrothermal theory unreasonable.

Before dealing with the paper systematically there is one further point to bear in mind, and that is Young's (23) statement on the gold in the bankets and its purely petrographic significance: "Neither pyrite nor gold can be regarded as essential constituents. Though normally pyrite forms from 2 to 3 per cent by weight of the Witwatersrand banket, and is visible to the naked eye, yet, on the other hand, it is sometimes present in very small amount, and is then quite inconspicuous. Gold, though confering great economic importance on the rock, is one of the rarest accessory minerals, and therefore cannot, from a petrological point of view be considered essential" (p. 80).

What does Davidson mean when he says (dealing with the uranium content): "The inference is, therefore, that the bankets are not sedimentary assemblages." The chromite, diamonds, zircons and tourmaline are all allogenic heavy minerals and according to Young the iridosmine and platinum as well, but the gold and uranium are introduced! Introduced so that in the Bird Reef Series, for example, the gold is small in amount, say less than 1 dwt/ton, the uranium oxide up to 0.2 percent, and in the adjoining reefs, gold is up to 10 times greater and the uranium oxide content is down. If there is a sympathetic relationship it certainly varies a great deal for each mine and for the various horizons.

I shall deal with the paper as follows:

1. The Transvaal-Southern Rhodesian Gold Province, the gold arsenic epoch (plus antimony) or rather epochs of undoubted hydrothermal origin, all in pre-Witwatersrand Rocks. The Witwatersrand gold-uranium ores and the minor constituents within the same province but much younger and different geological setting, contrast with these.

2. The gold distribution in any reef of hydrothermal origin and a comparison with the Witwatersrand, and say Tarkwaain bankets (Ghana).

3. Wall-rock alteration in hydrothermal deposits and its importance in such deposits in general.

4. Ore shoots in hydrothermal deposits all over the world, Kolar, Ghana, Southern Rhodesia etc.

5. The nature of the gold and uraninite in the Banket; the survival of various minerals.

6. Permeability of Witwatersrand conglomerates and adjoining rocks.

1. The Transvaal-Southern Rhodesian Mineral Province.—Emmons (5) has given a thorough survey of this province, which needs only revision in the light of more recent mining operations, and it is clear that the relationship between granites which are the host rocks of the gold, and the ores is a very common one. He even goes so far to point out that in the Lomagundi district gold is found in a conglomerate in the ancient schists series, but since they are associated with fractures and are found mainly near the contact of intruding granite, that the latter is probably the source of the gold. A conglomerate, therefore, can contain gold of hydrothermal origin. Before going any further it is well to bear in mind that Niggli (18) considered that the term "hydrothermal solution," for instance used without the defining adjective "magmatic," does not imply the solution was separated from a magma. The Alpine fissures he points out are hydrothermal formations that at the time of their formation were unaccompanied by magma. However, it is significant, that throughout this mineral province of gold-arsenic-sulfur, that magmatic rocks of a suitable nature intrude the gold-bearing formations, giving rise to pre-Witwatersrand mineralization. Note that arsenic is almost invariably an important constituent, antimony, copper, zinc and others are also important, and the mineralogy is comparable, for example, in the Cam and Motor in Southern Rhodesia and the Murchison Range (22). Yet when it comes to the Witwatersrand well within this province, a mineralizing magma (nor its derivatives) cannot be found, and in short space the ore becomes a gold-uranium-sulfur ore, with much rarer arsenic. A somewhat similar setting is found in Ghana where the Older Birrimian System contains gold deposits of hydrothermal origin—gold intimately associated with arsenic and sulfur, but in the Tarkwaain Bankets there is gold and black sands with water worn crystals of zircon and rutile, but according to Junner et al (11) "epidote, carbonate and pyrite are rare except near later dykes faults and quartz veins." The gold in the Ghana bankets is considered of placer origin and without a doubt the very close proximity of a long line of mineralization in the older Birrimian rocks of gold-arsenic-sulfur of undoubted hydrothermal origin but without any clear cut evidence of mineralization from a magma, gives weight to that theory.

In the case of the Transvaal-Southern Rhodesian Gold Province the pre-Witwatersrand mineralizing epochs, as far as gold is concerned, were arsenical, sulfurous in nature with lesser amounts of antimony, copper, zinc and lead. The gold in most seems to favor one type of pyrite, zinc blende, and arsenopyrite, whereas the galena has excess silver over gold. Now superimposed on these widespread deposits and in very extensive conglomerates in the Central and Southern Transvaal, S.W. Transvaal and the Orange Free State is the largest gold field in the world characterized by a conglomerate horizon with undoubted allogenic heavy minerals such as chromite, zircons, diamonds and in amounts less than the gold, irisosmine and platinum, but the gold and pyrite are introduced hydrothermally with uranium, the

latter being said to be sympathetic to gold. Once again note that the least important elements only are introduced, for it cannot be said that the pyrite is clearly of hydrothermal origin. Pyrite occurs in many sedimentary rocks without being introduced; its syngenetic origin is reasonably certain. Why has uranium only been introduced in Witwatersrand time and the arsenic, so prevalent over a long period of mineralization in pre-Witwatersrand times, is absent? The chemistry of the fluids is clearly not very different and the hydrothermal solutions whether magmatic or not must have come from these older rocks, bringing gold, sulfur, uranium but leaving behind arsenic, antimony, copper and zinc. Yet the older gold deposits are not notable for their uranium content, unless these older metamorphic rocks did not yield the gold, but the gold and uranium came from those notoriously poor mineralized pegmatites to form the greatest gold and uranium fields in the world.

2. The Gold Distribution in Reefs of Hydrothermal Origin and the Bankets.—The uniform distribution of the gold in the banket has been noted by many observers and although statements such as gold varies sympathetically with uranium have been made, no details have been published of sections along a reef. Nevertheless, I shall show that in the case of hydrothermal mineralizations, there is such a marked difference from the bankets, that some difference in origin must be postulated. In Table 1 I have taken some typical values of a gold-arsenopyrite hydrothermal mineralization. These values are characteristic of many such reefs and for long distances along the reefs.

Within this particular reef of milky to grey quartz there are argillaceous inclusions full of arsenopyrite, obviously wall rocks that have been included in the shear zone. These inclusions commonly carry good values, as do the wall rocks themselves. In this part of the drive good values have been found near the hanging wall contact but it is not an invariable rule. Within the wall rocks there is much mineralization as in most cases of hydrothermal alteration, and arsenopyrite, pyrrhotite, and dark types of quartz radically change the nature of the rocks. Gold values range from less than a pennyweight to 10 to 15 weights and in some places as high as 30 dwts.

Young (23) in his description of the gold in the banket shows that it is

TABLE 1

GOLD VALUES IN DWTS/SHORT TON. c = COUNTRY ROCK, q = QUARTZ

Values across the reef in dwts over width of sample in inches	Distance along the drive in feet						
	0	5	10	15	20	25	30
Hanging wall	5.0	73.2	4.4	5.6	7.2	3.8	2.0
	33 q	18 c	30 q	22 c	29 q	32 c	36 q
	2.0	9.4	8.0	1.0	103.0	12.2	5.6
	33 c	17 q	15 c	14 q	26 q	15 q	38 c
	7.0	9.2	3.0	103.2	4.6	6.0	
	30	14 q	20 c	22 c	21 c+q	17 q	
Footwall		11.2 q+c	1.0	2.6			
			16 q+c	20 q+c			

confined mainly to the matrix with very minor introduction into cracks in the pebbles, yet the main non-pebble quartz is secondary according to him. In hydrothermal mineralizations in fault and shear zones the inclusions, whatever the type, are mineralized and the wall rocks as well.

If gold and uranium, plus the pyrite were of hydrothermal origin it is difficult to understand why these have not been introduced into the adjoining wall rocks and inclusions. For example, first in the case of Konongo gold mines the mineralization of arsenopyrite, pyrite, pyrrhotite, and a little chalcopyrite is disseminated throughout the reef but is present to a *far greater extent in the wall rocks.*

3. Wall-Rock Alteration.—Hydrothermal deposits are characterized by wall-rock alteration to some extent or other and Schwartz has treated this in some detail. The wall-rock zoning may be far from regular and the enclosing shells may be much confused by veining along joints.

In the Transvaal-Southern Rhodesian gold province this is very common, for example Tyndale-Biscoe noted this in the case of the Central Part of the Mazoe Gold Belt, even where the country rock is a massive diorite, particularly in the richer parts of the ore body, the diorite is strongly impregnated with gold-bearing sulfides. The Konongo Gold Mine (also Bibiani) in Ghana has reefs very similar to those in the Barberton area of the Transvaal (17). In fact gold deposits of clearly hydrothermal origin throughout the world exhibit certain constant features from which qualitative rules can almost be deduced, yet these rules do not apply to the Witwatersrand ores.

Alterations have taken place in the banket, always due to some dike or sill and not due to a mineralizing solution that permeated along the conglomerate horizons. Wall-rock alteration is not conditioned by the permeability of the country rock for as van Eeden et al. (21, p. 78): "Arsenopyrite occurs in dense chloritic schists. At many localities along the Murchison Range it was noticed that wherever arsenopyrite occurs in small quantities with pyrite and pyrrhotite in a mineralized zone the arsenopyrite is usually restriced to the dense chloritic schists adjoining quartz veins with other sulphides." Sulfides occur in the hanging and footwall rocks of the bankets of the Witwatersrand (but note that in the Bankets of the Gold Coast are absent), and Davidson quotes Adam's figures of separating the pyritic seams and reefs of about 0.25 to 0.5 percent pyrite against 3–10 percent in the bankets, surely very clear evidence of a lack of wall rock alteration *between* mineralized horizons where in fact it should reach a maximum. In fact, pyrite occurs in many South African sandstones without any need to postulate a hydrothermal origin. A syngenetic origin for pyrite, that is the alteration in a sediment of a detrital iron oxide by sulfur precipitated in the sediment and subsequent reaction, is quite an acceptable hypothesis, so that the occurrence of pyrite in the quartzites above and below any particular conglomerate horizon is no proof of hydrothermal alteration, whether that has come from a magma or granitization process. It may well arise from connate waters within the sediment subsequently causing reactions between detrital minerals and their mineral content. In fact there is no reason from a sedimentary point of view why the quartzites should not contain more gold than sandstones of other geosynclines. If the

gold is of placer origin, then much of the sandstone material must have come from much the same source as the conglomerates, the difference being mainly in the transport. This does not conflict with the hydrothermal theory either for in the case of the Upper Birrimian rocks values of more than a trace of gold (about 0.1 dwt/ton in the case of the Witwatersrand and perhaps 0.2 dwt per ton or less in the case of more routine assays) but as much as 2.0 dwts per ton occur well beyond the zones of wall rock alteration and led Dixon in 1957 to postulate that the gold in the Konongo Mine might have come from the country rocks rather than a nearby granite.

Davidson goes on to say: "In South Africa the mineralization apparently dates from the period of post-Transvaal earth movements which gave rise to the Vredefort and other domes, accompanied by the Bushveld granite, alkalic plutons and nepheline syenite dikes." As the nepheline synite dikes are the ones that actually intrude the Witwatersrand in greatest quantity and are allied to the Pillansberg and Bushveld Complex, it is well to study them closely, particularly as regards alteration of the bankets where they intrude them and the possibility of these rocks transporting uranium and thorium.

Liebenberg has summed up this evidence showing that of 400 specimens of dikes none contained gold, although they carried sulfides and none were radioactive. In Southern Nyasaland, there are great numbers of solverbergite dikes (they are better described as micro-syenites) which originate from a large syenite body like the Pillansberg (Salanhdire), they traverse a line of brannerite-davidite mineralization along the Mwanza Fault and then enter the Tambane area of nepheline syenite gneiss where uraninite, monazite, allanite, zircons, davidite, columbite and much betafite occurs. The solvesbergite dikes are almost invariably weakly radio-active and would, according to Davidson, be the cause of the mineralization of these deposits of uranium and thorium, which lie in particular horizons of sedimentary gneisses. These are less continuous and uniform in uranium content than the gold in the Witwatersrand System, yet betafite for example is found well away from these dikes and where they cut the mineralized horizons there is considerable hardening and rock alteration but no uranium enrichment. The radio-active minerals have been dated and the monazite, davidite, and zircons yield an age of about 500,000,000 years. The solvesbergite dikes cut the Mwanza Fault (pre-Karroo in age but continuing actively until post-Karroo time) and then cut through the Salambidwe syenite complex, which is mainly non-radio-active and which is a syenite plug intruding the Karroo System (Bosazza, 1957). There are many strong reasons, therefore, why these syenite dikes could not have caused the mineralization, and in fact petrographic work suggest that their radio-activity is due to picking up from the rocks they traverse monazite and davidite, as well as allonite, which are widely distributed throughout the area. Commonly the solvesbergites are not radio-active over a short distance and that terrain has invariably proved barren in uranium and thorium.

Innumerable dolerite dikes that cut the same horizons and in direct contact with these minerals have not picked up any uranium. If the gold and uranium in the Witwatersrand System have been bought in by basic and syenitic dikes it is strange that in Southern Nyasaland where the same types

TABLE 2

SiO_2	26.95	38.60
Al_2O	26.20	39.06
Fe_2O	5.95	2.18
FeO	13.80	2.40
MnO	nil	trace
CaO	0.15	0.09
MgO	17.54	0.65
Ignition less	9.70	7.00
$-H_2O$	0.88	0.28
SO_3	not det.	1.74
	101.17	92.46

1. Vermicular chlorite from East Rand Mine with large piece of visible gold. Analyst, V. L. B.
2. Chlorite- sericite replacement of the Banket, Rose Deep Mine, collected by R. B. Young. Analyst, V. L. B.

of dikes occur and which traverse uraniferous country, they do not cause any mineralization but in fact may pick some up. In the Witwatersrand cases have been reported of basic dikes carrying visible gold and one example I examined from the East Rand showed large visible gold in a chloritic mass that may have been an igneous basic rock. In Table 2 the composition of this rock is given as well as the other in the Rose Deep Mine described by Young (23, p. 46).

The first sample contained several percent of gold at least, and according to Mr. W. van Biljon the mineral is slightly pleochroic from green to light green with the absorption of alpha and beta greater than gama. The indices in sodium light were alpha 1.610 and beta 1.618. This chlorite could be a result of a dike that has suffered great alteration in the vicinity of an auriferous horizon. The second material showed, according to Mr. van Biljon, mainly sericite with the following properties:

alpha	=	1.559	0.003
beta	=	1.591	
gamma	=	1.598	

The flakes were too small for 2 V. An assay made by Mr. H. Sommerville gave silver 0.6 dwt/ton and gold 0.50 dwt/ton. Of course one assay does not prove what has happened in this replacement of the conglomerate and after 30 years it was impossible to recover material, but as Liebenberg points out the gold in the Witwatersrand Banket is generally very regular in composition, so that this must represent a very unusual case. Nevertheless it shows what wall rock alteration can do.

4. Ore Shoots.—Nothing like the ore shoots of the Kolar Gold Field have been observed in the Witwatersrand. Note that Kolar is one of the few large continuous gold fields in the world, and the gold is considered to be hydrothermal. The ore shoots in that field and many others have no resemblance in the Witwatersrand Mines (19). There is not a gold deposit in the world that does not show such ore shoots, notable for example are the hydrothermal deposits in the Birrimian rocks of Ghana and the lack of such ore shoots in

the bankets. Of course there are variations in the gold content and hence the payability, but it is the remarkably uniform nature of the Witwatersrand ores compared with "the erratic distribution of the ore shoots and of the gold within them," of the Kolar gold field that is striking.

Within ore shoots such as those of the bankets of Tarkwa and Abosso, there are small enrichments in bedding and oblique faults, that have been used by Kransdorf (13) to consider that the Rand bankets owe their gold to hydrothermal solutions, rather than a placer source. In the first instance Kransdorf has omitted to say that the Tarkwa and Abosso bankets do not contain sulfides but oxides of iron, and it would be daring to say that in this one deposit that gold has been introduced hydrothermally without bringing in any sulfides to react with the black sands (haematite) of the bankets.

In the Konongo gold mines and other Ghana gold mines there are innumerable small faults, commonly with some visible gold in chlorite partings in the fractures. They rarely extend beyond the width of the displaced quartz reefs and are purely local affects probably contemporaneous with the mineralization in some cases but in others somewhat later. They do not indicate in any way the main hydrothermal mineralization in the Konongo Mine. I cannot see that similar faults have great significance in the Witwatersrand Mines as they are only common in the case of the Randfontein Estates and a few other mines. They merely indicate a metasomatic change in the bankets, which in fact no one has ever denied but they do not indicate that solutions from a magma or granitization area have entered the conglomerate bands. As Liebenberg (a point made generally by Knight (14, p. 815) puts it so well in the following words (15, p. 205): "The absence of positive channel ways for the late introduction of gold-bearing hydrothermal solutions into the Witwatersrand System is an important point raised in the past to discount the hydrothermal theory." In the Upper Birrimian rocks of Ashanti there is continuity for miles of the faults planes both graphitic and non-graphitic, yet the ore shoots rarely are more than some hundreds of feet at any one particular level along the strike. For over 100 miles from north-east of Konongo south-westwards, gold mineralization has been proved, indeed not a small structure, but no Witwatersrand continuity has been found even in any one mine. Liebenberg goes on to say: "This mode of origin of the gold also explains the presence of gold in the banded pyritic quartzites and disconnected lenses of conglomerates . . . ."

In terms of ore shoots the Witwatersrand consists really of three vast ore shoots (1) the Far East Rand Extension (2) the Main Witwatersrand mining area and the offshoots in the far West and Klerdorp areas and (3) the Orange Free State. The paystreaks of the East Rand are not comparable with the ore shoots of hydrothermal deposits, for one thing their dimensions are far greater than any ore shoots known (4, p. 108). They coincide with sedimentary features, whereas ore shoots start and stop both laterally and in depth without any such controls.

5. The Nature of the Gold and Uraninite in the Banket, and the Survival of Various Minerals.—Much has been made of the hackly and micro-nuggetty nature of the gold in the Banket, as opposed to a rounded nature that it should

have if of placer origin, but in fact many detrital gold grains do not have a well rounded nature (11) and this particularly applies for example to nuggets. Junner examined alluvial gold from the streams in the Ankobra System and found the bulk to be sharply angular or only slightly water-worn. As a general rule it can be said of any mineral or rock fragment that the larger it is, the more readily it is rounded, therefore nuggets in a placer deposit should be well rounded but in fact are often not. Then there is the question that gold, the most ductile of metals, malleable and yet tough, yields to forces and assumes all sorts of shapes. In this it behaves like the clay minerals of sediment that do not have the shape obtained during transport, but on consolidation change completely. The bankets must have taken a tremendous amount of compaction before being finally completely cemented by secondary silica, and gold, which as a very minor constituent, could not have played any dominant part in the structure of the rock but must have been subordinate to the other harder and more abundant minerals. With regard to the rounded nature of the uraninite I agree with Davidson that this is no proof of the possible syngenetic origin for the simple reason that uraninite could not have been anything else but an equidimensional grain of nearly rounded nature. Most of the uranium minerals crystallize in the cubic system and some like betafite are hexoctahedral. What is the difference between a grain of 50 microns diameter comprising the cube and octahedron perhaps rhombic dodecahedron, and a rounded grain of the same size, particularly if the faces are poorly preserved, dull, and hence poorly reflecting. It would have been strange indeed if the uraninite had not been of a rounded nature. I have thin sections of the chromitite of the Bushveld Complex in which the chromite grains are as well rounded as the uraninite in the banket.

Neither is the argument relevant that quartz and feldspar do not round well below say 150 microns, for it is a fact that in sands and clays of wind-blown or water origin, that quartz and feldspar do not round well below 150 microns and not at all below 74 microns. On the other hand in the course of examining many hundreds of size fractions of soils, clays, loesses, and sands that have been worked by rivers, wind, and beaches, I have never seen ilmenite, magnetite, and chromite that are not equidimensional and rounded, and mainly less than 74 microns in diameter. It has been pointed out by Holmes that in the rivers of Niassa, that oolites of iron oxide are formed and transported quite readily, and in fact there is no reason why uranium oxide could not have been transported in that condition, for iron oxide is just as soft and readily soluble in acid waters. I am referring here to tropical river waters of high temperature and generally high acidity, yet such transportation is taking place according to Holmes. In fact I have observed such oolites in sediments.

Then there is the question of replacement, for uranium is able to replace say phosphates, and pellets of phosphatic material are by no means uncommon. I have seen pellets and small pebbles of clay materials transported by rivers into the bay of Lourenco Marques. Some of these pellets contained a great deal of black organic matter. Twenhofel (20) for example quotes data showing that oolitic phosphorites can contain from 33 to 36% P. 205 (p. 548).

That something of this sort can take place is illustrated by the betafite oc-

currences in the Tambane area, Southern Nyasaland, which I have examined in detail in the field and in the laboratory. The betafite in general occurs in rounded grains in places showing an oolitic structure, with rounded ilmenite and rounded zircons. There is a second generation of zircons in larger pyramidal crystals and the same applies more rarely to the betafite, which occurs in veins of biotite in crystals of about 203 cm. diameter, the cube, octahedron, and rhombic dodechedron being present. From both field structures, the nature of the rocks and the detrital minerals present, there is little doubt that whether nephelinized or not, the Tambane syenites are metamorphosed sediments, with a very complicated history of metamorphism. The most reasonable hypothesis for the origin of the uranium minerals is that they are the reaction products of uraninite on columbite and ilmenite grains resulting in a betafite and davidite mineral deposit, in which the minerals have a very variable composition. Mainly the original detrital grain forms have been preserved but in some cases larger aggregations amounting to large boulder size, of columbite and uraninite occur. Massive uraninite occurs in the deposits.

Davidson has mentioned the Gold Coast (Ghana) in his list of placer deposits examined. Kitson and Felton (12) examined some 639 samples from stream gravels, soils, and crushed rocks of the Gold Coast (Ghana) and it is interesting to note in that hot humid climate that the following (some unstable) minerals were found, with the frequencies shown:

Total of 639 concentrates examined

No. of Times Found	Mineral	No. of Times Found	Mineral
605	Zircon	11	Pyroxene
247	Epidote	5	Arsenopyrite including lollingite
153	Amphibole	2	Pyrrohitite
127	Haematite	1	Copper
127	Limonite	1	Chalcopyrite
29	Pyrite	11	Galena
26	Cassiterite		

Some of these are from outcrops of "igneous rocks" but in the main they are from streams. It is not unusual in Ghana, in the high rainfall areas to find depths of complete decomposition to as much as 200 feet vertically, and 50 to 60 feet is quite general in the case of the phyllites and graywackes. That minerals such as epidote, amphiboles, and pyroxenes should persist in such a harsh climate indicates that it is a long way to go in geology before one can postulate invariable rules. For example, I have pointed out that many minerals obtain a protective coating during weathering and then there is the converse of that when certain clay products for example, become active agents according to Graham (6). During transport also, other factors must be considered and the conclusion that certain minerals are not present in alluvial deposits is only valid when it is shown that in the drainage area that mineral is common and is not too diluted to be detected in subsequent alluvials. For example, around Tambane Nyasaland there is abundant corundum, which is a very persistent mineral, yet in dozens of concentrates, in fact a few hundred,

examined from below that area corundum has not been observed. This is due to the great dilution by more abundant minerals downstream.

The fact that in the rivers of near equatorial regions rounded iron oxide can be formed and transported in rivers is worthy of further study and also trace quantities of the soluble materials. At Tambane uraninite has been found in outcrops with only minor quantities of secondary minerals, both in large boulders of the mineral and small grains. It is at the rock outcrop that most chemical decomposition takes place and not so much during transport.

6. The Permeability of the Witwatersrand Bankets and Adjoining Rocks.—It is generally assumed that conglomerates are more permeable than sandstones, but much depends upon what fills the voids of conglomerates and the purity of the sandstones. If, for example, a sand is deposited of fairly pure quartz and subsequently a pebble bed of uniform pebbles is laid down on this, then the sand is bound to be a little more permeable than the conglomerate as the volume taken up by the pebbles is impermeable. The more clay material in the sand the less permeable it becomes. The same applies to the conglomerate bed above. The Witwartersrand quartzites in the Upper and Lower Division are remarkably pure in most cases. The bankets of the Witwatersrand are more argillaceous than the quartzites. Young (23) quotes analyses showing banket ore containing 86.78 percent silica and Bastard reefs even lower with 73 percent silica and correspondingly higher alumina. Many of the quartzites contain well over 90 percent silica.

Young (23) has pointed out that: "The identity of the pyritic bands with the banket matric is clearly demonstrated when, as occasionally happens, pebbles appear in the bands and the rock passes into a typical banket. There can be little doubt that what are now pyritic bands were at one time layers of sand, in which a certain degree of concentration of heavy minerals has taken place, as in the pebbly beds. It would be well if those advocates of the infiltration theory of the genesis of the gold in the banket, who lay stress on the original greater permeability of the banket compared with the associated quartzites, would turn their attention to the banded pyritic quartzite."

In fact Davidson notes that in Blind River that there are important developments of radio-active quartzites and grits that have as high a uranium content as the conglomeratic ores but are devoid of pyrite. These mineralized quartzites where the conglomerates are locally absent from the succession occupying the same stratigraphical horizon as the latter. The problem of infiltration is that it could only have taken place well after the completion of the deposition of the Witwatersrand System, when small contemporaneous faults in the banket horizons had taken place, and larger ones as well, compaction that had started at the time of deposition must have been advanced, and by then certainly some secondary silicification had taken place.

Radio-active dating is not very useful at this stage, but if the age of 620,000,000 years is considered for the uraninite, suggested by Dr. Davidson (p. 688), by then the whole of the Witwatersrand System was well compacted and metamorphosed and that mineralization along the banket alone would have been impossible, diversions along joints, faults and dike walls would have taken place. Wall rock alteration, other than the migration of rutile

into the quartzites postulated, would be noticeable and many other effects. By that date in fact the Witwatersrand System had a complex system of dikes, and only a magmatic body in close proximity and undoubtedly showing relationship to it, could have effected such mineralization.

There are many difficult problems associated with the genesis of the Witwatersrand, and Davidson's critical reviews in the post-war years have done much to stimulate new thought. What is required is far more detailed geological sections across the system from the East to the West Rand, more quantitative petrology of the bankets and beds below and above, and details of the distribution of the gold and uranium in the bankets in one horizon, and the relationship of one horizon to another. This latter data must be available in many of the mine records, not only for the uranium producers but for others as well. The values so far published in company reports, and statements that the two elements vary in sympathy are not sufficient for a real assessment of the subject.

The crux of the problem is that put in Young's words that the gold (and this can be applied to the uranium) are only very minor constituents of the banket and that the more abundant ones are mainly of undoubted detrital origin. Only the uranium, gold, and perhaps the platinum metals can be considered hydrothermal. Even the very rare diamonds are detrital, but if the infiltration theory is accepted then we must make an exception for these.

I can only appeal to Bernard Shaw's Pygmalion to express my thoughts adequately.

Dr. R. A. Pelletier, Consulting Geologist to New Consolidated Gold Fields Ltd. kindly gave permission to publish the data on the uranium minerals in Southern Nyasaland.

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THE OCCURRENCE OF URANIUM IN ANCIENT CONGLOMERATES

(*by C. F. Davidson in this Journal, 1957, No. 6, p. 668–693*)

Sir: One of the interesting facets of geology (and one which labels it as an inexact science) is that one observer can offer a theory on a particular subject and make it sound utterly convincing while another can study the same subject and come up with a diametrical solution that also seems utterly convincing. A case in point is that of the origin of the auriferous-uraniferous conglomerates of Proterozoic age which occur on the Witwatersrand (South Africa), in Blind River (Ontario), in Rum Jungle, Australia (Crater Beds) and on the Sierra de Jacobina (Brazil). Arguments on the origin of the gold (and more recently the uranium) in the Rand bankets have been rife for over 60 years, the arguments being between geologists who have worked on the bankets and who are generally placerists and visitors and armchair observers in other lands who are, in the main, hydrothermalists.

Dr. Davidson in a recent paper in this Journal (Vol. 52, pp. 668–693) implies that the papers by Ramdohr and Liebenberg are the last dying gasps of the placerists and goes on to "disprove" their theories and those of others on geochemical grounds and on the grounds of noncompliance with Lyell's Doctrine of Uniformitarianism. Of late it has become standard practice to solve geological problems by turning to microscopy, geochemistry, age determinations and the like, in preference to field evidence. In some instances seemingly authoritative papers have been based entirely on the examination of specimens without the writer having visited the area or even the country of origin. The present writer expected an outcry from "those concerned with day to day

mining operations" but since few appear to be forthcoming, the following remarks are offered, lest anyone think that placerism is dead.

It is true that most of the old arguments supporting one theory could be given different interpretations and made to support the other theory. Of the newer methods of attack, even Davidson admits that age determinations can be misleading and at the same time he admits that later remobilization has definitely taken place, thus giving support to the placer hypothesis. His argument that uraninite is not a placer mineral appears a good point and his innumerable examples seem overwhelming. It is hard to refute his arguments in either the Blind River camp or the Rum Jungle area (both of which the present writer has visited) but on the Rand there is irrefutable field evidence that proves conclusively that the placer theory is the only tenable hypothesis.

For the benefit of those not conversant with the Witwatersrand field the following brief description is given.

The Witwatersrand sediments comprise a thickness of up to 30,000 feet of water-lain rocks that lie on an older granitic basement. They have been divided into an Upper and Lower (older) Series. The latter are, in the main, a fine-grained series of shales and "dirty" quartzites, whereas the Upper Series comprise clean siliceous quartzites with some sericite but little chlorite, numerous conglomerate beds and two main shale horizons, the Jeppestown and Kimberley. The individual conglomerate groups such as the Main, Livingstone, Bird, Kimberley and Elsburg are ideally present around the rim of a basin some two hundred miles in diameter that passes through the towns of Johannesburg, Randfontein, Venterspost, Klerksdorp, Odendaalsrus, Heidelburg and Springs.

Individual horizons in the Main Reef group have been mined fairly continuously over lengths of 100 miles in the original Johannesburg area. Over lengths of 20 to 30 miles individual horizons can often be distinguished, one from another, by macroscopic examination of specimens by European and African samplers. Size, color and shape of pebble and matrix, size and distribution of pyrite buckshot are generally quite distinctive. So are associated overlying markers such as narrow bands of fine-grained siliceous quartzites and yellow sericitic shales. In general, economic quantities of gold and uranium occur in certain of the siliceous well-sorted horizons but poorly sorted horizons with argillaceous matrices are invariably barren. The fact that the ore minerals are confined to certain conglomerate bands, in places only a half-inch thick, suggests that the ore was deposited in these horizons by placer processes.

Unconformities and local washouts are extremely uncommon and it is apparent that the reefs were not laid down individually on an alternately rising and subsiding coastline but that the pebbles were washed out by some agency and possibly deposited on a subsiding geosynclinal continental shelf.

A period of erosion followed the deposition of the Upper Witwatersrand Series and a basal conglomerate called the Ventersdorp Contact Reef was formed in river courses on this old land surface (1). Probably prior to and during this erosion period, faulting took place and ultimately the Ventersdorp

Lavas were extruded, probably via these major faults since amygdaloidal dikes of Ventersdorp diabase composition are present in the vicinity of the strong Witpoortje Fault on the West Rand (2) (Fig. 1). This fault is of major dimensions having in places a throw of plus 15,000 feet. Mining of this Ventersdorp Contact Reef is local and not widespread.

Another period of erosion followed the Ventersdorp period and onto this eroded surface was deposited the Black Reef followed by dolomites of the Transvaal System (also of Proterozoic age). Payable Black Reef on the West Rand is confined to strike depressions representing the weathering out of softer horizons such as the Jeppestown Shales, but on the Far East Rand excellent values occur in deep river channels cutting into the Witwatersrand rocks. In either case the later Black Reef is similar in appearance to the Witwatersrand reefs except that there are more and larger buckshot pyrite "pebbles" (mainly concretions).

These Black Reef conglomerate stream channels (up to 100 ft. thick) on the Far East Rand are incised deeply into the underlying Witwatersrand rocks. Downstream of a particular Witwatersrand conglomerate, large blocks of this same conglomerate can be recognized for hundreds and even thousands of feet. If this particular Witwatersrand reef contains gold, then so do the boulders in the Black Reef and vice versa, a barren Witwatersrand reef provides barren boulders to the Black Reef channel.

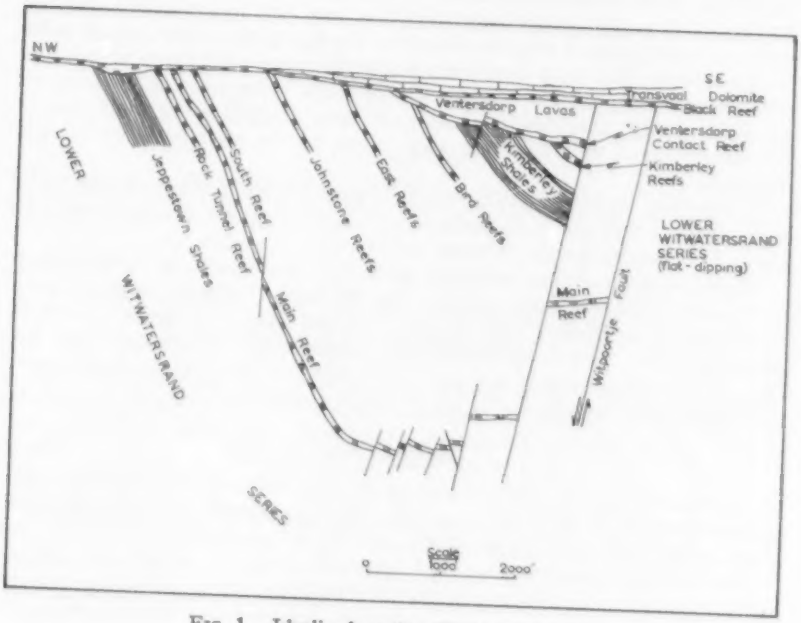

FIG. 1. Idealized section West Rand area.

The occurrence of gold and uranium in the Black Reef is generally confined to a limiting distance of ½ mile or so from the sub-outcrop of a payable Witwatersrand reef.

ORIGIN OF THE GOLD AND URANIUM

Most geologists will agree that the above evidence from the Black Reef suggests that the gold was present in the Witwatersrand conglomerates prior to the deposition of the Black Reef and that the gold, uranium, and pyrite in the Black Reef were derived from the Witwatersrand rocks by a placer process. When shown this example in the field very few geologists offer any alternative argument.

There is one more argument that appears irrefutable and is supported by Lyell's Doctrine of Uniformitarianism.

The hydrothermalists argue for one period of mineralization, which has to be post-Black Reef. Now look at Figure 1. Compliance with their theory would mean that faults of huge dimension were present when the gold was introduced. This seems to be very unlikely since:

1) the well-known payshoots of the East Rand are offset by faulting. When these faults are "rectified" the payshoots fit together like jig saw puzzles. There is little doubt that the faulting is post-gold.

2) if these countless millions of ounces of gold and uranium were introduced into these rocks hydrothermally then surely, in the presence of such intense faulting, we should have found at least one hydrothermal gold or uranium quartz-bearing vein somewhere in the hundreds of thousand of miles of development that have been done in the Witwatersrand beds. Such has never been found, the only ore known on faults being in isolated pieces of normally payable conglomerate that have been dragged along fault planes. Re-distribution of gold has been very minor, as the placerists have always maintained.

Surely we would expect to find gold-quartz veins present on the Witwatersrand as they are in undoubted hydrothermal camps, if a hydrothermal origin were correct for the Witwatersrand.

Again, if gold-uranium solutions passed up these faults we could expect enrichment in payable conglomerates near the faults. Also we should expect enrichment in normally "unpay" conglomerates near such faults. Such is never the case. A well-sorted siliceous conglomerate, particularly near the base of a series commonly contains gold while overlying poorly sorted conglomerates (just as porous) do not generally contain gold.

CONCLUSIONS

The above remarks refer mainly to gold but since uranium is intimately associated with gold and undoubtedly has the same origin there is little doubt that a reference to gold could equally well refer to uranium.

Geology has always been and probably always will be an inexact science. Field observations and relationships that are obvious to the naked eye and to good old-fashioned common-sense should be accepted in preference to geo-

chemical evidence and to age determinations, since the rocks and minerals concerned have generally been subjected to many later metamorphisms. Geologists of today are forgetting the importance of field evidence.

In the case of the gold-uranium bankets there is little sound evidence for either theory in Blind River, Rum Jungle or the Sierra de Jacobina but field evidence from the Witwatersrand is overwhelmingly in favor of the placer hypothesis.

Whether the pyrite in the bankets is of placer origin or whether it is derived from sulphidization of detrital black sands is an enigma. One would expect to find some black sand if the atmosphere was an oxidizing one. However, syngenetic pyrite is quite common in Precambrian sediments, particularly graphitic ones, in Canada and in Australia (Nairn pyrite deposit) and it is possible that the organic matter that later produced the hydrocarbon thucholite, from uraninite would produce reducing conditions in these bankets for the deposition of pyrite and not iron oxides.

Future research on the geochemistry and ages of these bankets will probably add little but confusion to the picture. What is really needed is research on sedimentation, and particularly on the origin of conglomerates—rocks that are little understood. If the conglomerates were deposited on a subsiding continental shelf, as seems likely, then how did the pebbles get out that far, and how was the gold transported to this locale. Alternate submergence and uplift is unlikely since local disconformities and "washouts" are the exception.

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RELATIONSHIP OF ORE TO PORPHYRY IN THE BASIN AND RANGE PROVINCE

Sir: The transition from qualitative to quantitative research in the geological fields of endeavor shows a marked contrast with that in most spheres in that it is still in its infancy. Thus, we welcome contributions of the nature of that presented by Bronson Stringham (ECON. GEOL., Vol. 53, No. 7). The change in attitudes that becomes apparent during the swing-over from geological science to the art of applied geology, with its actuarial overtones, is apparently most difficult. It is for this reason that we should examine with unusual care every technique of application of the statistical method. All terms used must be subject to minute scrutiny if progress is to be made in this, the quantitative phase of applied geology.

TABLE 1

No.	Term	Context	Restricted definition[1]
1.	Aphanitic	A. matrix A. groundmass	Mineral grains are too small to be perceived with the unaided eye (Stringham, p. 809)
2.	Associated (synonym: affiliated)	A. mineral deposit	Within 2 miles of the intrusive aphanite (Stringham, p. 819)
3.	Barren	B. intrusives	Salic plutons in whose immediate vicinity there is no epigenetic mineralization of commercial interest (Bichan)
4.	Exploration Area	Within 2 m. of the E. A.	Potentially a mining district (q.v.) and of no specified size (Bichan)
5.	Granitoid	G. textured rock G. intrusives	All minerals are visible to the unaided eye (Stringham, p. 809)
6.	Large (synonyms: extensive)[2]	L. aphanite L. ore body L. district	See more detailed account under Table 2
7.	Mining District synonym: mineralized district)	General	A mineralized area from within which there have been (or will be ?) produced "over $3,000,000 of (metallic values)" (Stringham, p. 808)
8.	Ore Body (synonyms: ore deposit; economic mineralization	A significant O. B.	See more detailed account under Table 3
9.	Porphyry Pluton (synonym: aphanite[3] with phenocrysts)	Productive and barren P. Ps.	Rocks possessing an aphanitic groundmass and visible phenocrysts (i.e., visible to the naked eye?) (Stringham, p. 809)
10.	Productive	P. intrusives	Salic plutons in whose immediate vicinity there exists epigenetic mineralization of commercial interest (Bichan)
11.	Reasonable Expectation	R. E. of a significant ore body	86 percent (Stringham, p. 806)
12.	Significant (synonym: economic)	S. mineralization S. ore body S. amount	To the value of "over $3,000,000" (Stringham, p. 808)
13.	Small	S. dike S. intrusive S. sill	See more detailed account under Table 2
14.	Very (Large)	V. large outcrops	See more detailed account under Table 2

[1] I.e., in the sense of its application to the subject-matter of the article under review.
[2] Also: sizable.
[3] I.e., in the sense of the porphyry-ore association, it is apparently equally an aphanite-ore association (with or *without* phenocrysts).

The use of *hydrothermal* in the Stringham paper is deemed inessential at this stage of the investigation; *epigenetic* seems to me less subject to misinterpretation in its implications. Thus: "productive" intrusives are "those associated with *epigenetic* mineralization."

Through a preoccupaton (essential to one's living) with the practical applications of the results of statistical research, rather than the philosophical disquisition thereof, I have found it useful to assemble the following table of definitions. Where the meaning is not apparent from the body of the Stringham contribution, I have taken the liberty of supplying my own concept of the term used.

The use of the terms "large" and "small" with qualifying adjectives, comparatives and superlatives, is all-too universal to be left to the individual choice of the investigator any longer, especially when in reference to specifics such as:

Aphanite	Ore Deposit
Igneous Body	Outcrop
Intrusion, Intrusive	Porphyry (Body)
Mining District	Proportion
Ore Body	Sill
	&c.

It is therefore encouraging to find that Stringham has made a start in the definition of specific cut-off points between the *large* and the *small*, as applied to dikes and sills, plutons, and mining districts, and that with the latter he has been yet more specific and sub-divided them into no less than five categories that might with some justification run the gamut from those of *minimum* size, through *very small, small, intermediate,* and *large,* to *very large.*

According to Stringham:

	small	*large*
Dikes and Sills	under 100 feet	over 100 feet *thick* (p. 814)
Plutons	under 1,000 feet	over 1,000 feet in *smallest dimension* (p. 818)

and for Mining Districts, the limits as shown in Tables 2, 3, and 4 (Stringham, p. 814–816, inclusive) are specific:

TABLE 2

Designation (Bichan)	Limits ($ value of past production)[1] (Stringham)
Minimum	under $3,000,000 (Bichan only)
Very Small	over $3,000,000 and under $5,000,000
Small	over $5,000,000 and under $10,000,000
Intermediate	over $10,000,000 and under $25,000,000
Large	over $25,000,000 and under $50,000,000
Very Large	over $50,000,000

[1] It also appears reasonable to me to apply these same size designations to *exploration areas*, or to *mining districts*, with the same given amounts of *reserves* as those shown in the table of production figures (Table 2); since I am at present engaged in a *mining district* with *both* very large past production, *and* very large current reserves, I am struck by the necessity for considering exploration areas in the same light as known mining districts.

Although some of the foregoing terms, e.g., *aphanitic* and *granitoid*, are well-defined and universally understood throughout the profession (of applied

geology), and essential to any clear-cut progress from the end-point of the current Stringham paper, I believe that additional definitions, including the dozen added above, are no less vital to an avoidance of the *"inconclusive reporting"* that has apparently hampered the author in his previous investigations into the *porphyry-ore* (*aphanite-ore*) associations.

The empirical relationships have been well summarized. As Stringham doubtless knows, although he is prone to avoid the global connotations at present (p. 807), the association is by no means confined to observations in his chosen territory.

The prime question is: can the proximity of ore to aphanite, on the one hand, and the mutually exclusive occurrence of granitoid rocks and ore (with the exception of tungsten, as noted by Stringham, p. 806, and certain specified districts, which could perhaps have been segregated into a separate table), be attributed to the presence (or the absence) of unique characteristics of rocks that have either been cooled rapidly (i.e., have entered an environment possessing an elevated temperature), or have been allowed to cool slowly?

Previous references to the porphyry-ore association (p. 820) are, by design, insufficiently exhaustive to do more than suggest some partial answers to the implied questions. The one point of encouragement lies in the fact that *both* the strategic *productive* and *barren* plutons (p. 808) may correctly be included amongst those "regional structural elements that have been mapped by the geologist" (W. James Bichan, 1957, Econ. Geol., Vol. 52, p. 100).

This contributor has previously divided the pre-ore conditioning factors into those "primarily geological, mechanical, physical or chemical in origin" (*loc. cit.*, p. 101). Some questions are suggested by Stringham's penultimate paragraph, Geological Processes Involved (*loc. cit.*, p. 820):

(1) If none of the factors enumerated above have been operative, is there likely to be any epigenetic ore present?

(2) Similarly, if any one of these factors has been inoperative, will there be ore?

(3) Why is the presence of an aphanitic pluton a pre-condition for epigenetic mineralization?

(4) Is the presence of an aphanitic pluton, or in fact a pluton of any description, a pre-requisite in the ore environment?

(5) Which of the enumerated factors are brought into play as a result of, or as an unavoidable accompaniment with the entry of an aphanitic (or any type) of pluton into a specified environment?

These are some of the questions that remain to be answered before we can know what weight to attach to the presence (or absence) of the aphanites, or the granitoid plutons, in any areas chosen for special exploratory investigations.

All of the variable factors discussed by this contributor (*loc. cit.*, p. 102) are vitally affected in various ways when igneous plutons enter that portion of the earth's crust chosen for critical appraisal with regard to its ore-bearing

potential. The question is thus but one aspect of the whole problem of ore genesis. The statistical approach is going to be of extreme value, but the end of these investigations is very, very far from being within view.

The further allied question of what constitutes an ore body may be related to the limits set out in Table 2 of this contribution. It is clear that total size can have a bearing, and that what once could be considered as an ore body (under the unitized operations of years' past) may perhaps not qualify today. Thus the minimum Mining District of Table 2 could have contained what would have been termed ore bodies a century ago: deposits that could be and, in fact, were worked for their valuable metallic content. What constitutes an ore body today? I must confess that I cannot place a figure upon the requisite minimum, neither as to tonnage, nor as to aggregate value, for no one of the metals concerned, neither for any of the non-metallics. If any one else can set up Table 3, briefly-noted under 8 (Table 1 of this contribution), they will doubtless earn the undying thanks of all commercial geologists, but the data is, by the same token, likely to become outdated before the ink is dry. It is worth an attempt.

As a finale, I cannot go along with what Stringham has "safely . . . concluded," namely:

> the geological processes which make or form an intrusive aphanitic textured rock . . . are also capable of forming associated economic hydrothermal (*epigenetic*) ore deposits, and further that the geologic processes which form a granitoid rock . . . are *not* capable of forming large hydrothermal ore deposits" (*loc. cit.*, p. 820—parenthetic addition in italics is this contributor's comment).

The operative word in this connotation is undoubtedly the equivocal term, *large*. If the author will concede that a mining district with past production or current reserves in excess of $25,000,000 is indeed large (Table 2 hereof), I would venture to suggest that he will have little distance to travel to note more than one such area within the continental United States, and more than a score the world over.

In closing, may I state as my considered opinion, that there is no such pluton as a barren intrusive, if the phrase *"immediate vicinity"* be taken in the same sense as Stringham's *associated* (i.e., within a radius of 2 miles): there are only barren horizons relative thereto (unfortunately they are commonly the ones coincident with the present-day land-surface).

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ORIGIN OF THE NAIRNE PYRITE DEPOSIT

Sir: The origin of the Nairne Pyritic Formation has been disputed for many years, and the question has been brought up again by B. J. Skinner (7) in this Journal. Edwards and Carlos (2) considered that the deposit

was of hydrothermal origin. However, subsequent investigations, especially that of Skinner (7), tend to show that the deposit is of sedimentary origin. As Skinner points out, the compatable relationships displayed between ore and gangue minerals, and the fact that this sulfide-bearing formation can be traced for more than 65 miles, are very strong arguments for a sedimentary origin.

Recently much attention has been focused upon the formation of such sedimentary deposits. Skinner's theory is rather unique and could affect the interpretation of other similar ore deposits. It should therefore receive close attention. Skinner believes that the sulfides were deposited in a shallow water environment, and then later re-deposited in a deep water basin. His main arguments for this theory are that the grain size of the sulfides reflects the grain size of the enclosing rock minerals, and that he has found graded bedding, with similar size sorting. That the sulfides are not detrital is rather apparent—sulfides are not that resistant to weathering. Instead, as Skinner suggests, they were probably deposited by chemical precipitation, possibly as hydrous iron sulfides; these were subsequently recrystallized during metamorphism. However, that they were re-deposited in a deep water environment is not only difficult to believe, but also unnecessary. Skinner places much weight on the graded bedding he has found in the formation. Graded bedding, such as this, could have been caused, he argues, by turbidity currents (p. 561). He next deduces that the Nairne formation was deposited by turbidity currents (p. 561). He has, however, found graded bedding in only 5 percent of the sediments and these beds range from 1 cm to 4 cm in thickness (p. 549.). Turbidity currents such as those that flow out into the ocean deep arise on the continental shelf. Loose sediment, mixed with water, is shaken free by, say an earthquake, and rolls down into the basin, producing graded bedding (1). If the entire Nairne formation had been deposited in this way one would expect more than 5 percent of the sediments to display graded bedding. The 1–4 cm thickness of each bed might also be open to question.

Skinner's other main argument is that the grain size of the sulfides reflects the grain size of the enclosing rock minerals. True as this may be, it need not be caused by turbidity currents. Seasonal fluctuations in sedimentation and precipitation might also be the cause. Moreover, it could easily be a phenomenon dependent on metamorphism: the sulfide grains would tend to grow to the same size as the gangue minerals in the immediate vicinity.

Skinner also states that the sediments could not have been original black muds (p. 561). Why this is so is not clear. Black muds are black essentially because they contain carbonaceous material or finely divided sulfide material. The Nairne formation evidently contained sulfide material, hence they were probably original black muds. Also, carbonaceous material, transformed during metamorphism into very fine-grained graphite, is present in the gangue (personal microscopic observation).

Thus, from the above discussion, it is rather difficult to accept Skinner's theory of re-deposition in a deep water environment. It seems, instead, that the sediments probably were deposited "in situ". The estimated 5 percent

of the sediments that contain graded bedding could easily be a minor and local feature, and sulfide-gangue grain size relationships may be ascribed to causes other than turbidity currents.

The actual sedimentary environment of such deposits is also of interest. Krumbein and Garrels (5) examined the Eh and pH controls in detail, as well as such controls as composition, pressure, and temperature. In their classification (p. 26), the Nairne deposit would fall below the sulfate-sulfide fence (below approximately Eh = −0.2) and between a pH of 7.0 and 7.8. Such sediments form in areas of restricted circulation under strongly reducing conditions and in the presence of anaerobic bacteria. The characteristic assemblage is organic matter, pyrite, and phosphorite. Organic matter and pyrite have already been mentioned and locally the formation contains as much as 2.2 percent phosphates (unpublished South Australian Department of Mines analyses).

Because the formation has undergone metamorphism, it is difficult to deduce the nature of the original sulfides. The fact that pyrite and pyrrhotite are present in roughly equal proportions may or may not be purely a function of metamorphism. Huber (4) has calculated an "FeS" stability field below that of pyrite. Rosenthal (6) has produced pyrrhotite synthetically at room temperatures with low sulfide ion concentration (sulfide ion concentration decreases with decreasing Eh) and Erd et. al. (3) have discussed the low-temperature origin of smythite (Fe_3S_4) and pyrrhotite in sedimentary rocks. If both "pyrite" and "pyrrhotite" did originally form, then, according to Huber's diagram (p. 131), the Eh value at the site of deposition may have been as low as Eh = −0.5; this, of course, is speculation.

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ADELAIDE, SOUTH AUSTRALIA,
Nov. 29, 1958

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2. Edwards, A. B., and Carlos, G. C., 1954, The selenium content of some Australian sulphide deposits: Australian Inst. Min. Met. Proc. 172, p. 31–63.
3. Erd, R. C., Howard, T. E., and Richter, D. H., 1957, Smythite, a new iron sulfide, and associated pyrrhotite from Indiana: Amer. Mineralogist, v. 42, p. 309–333.
4. Huber, N. K., 1958, The environmental control of sedimentary iron minerals: ECON. GEOL., v. 53, p. 124–140.
5. Krumbein, W. C., and Garrels, R. M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: Jour. Geol., v. 60, p. 1–33.
6. Rosenthal, Gernot, 1956, Versuche zur Darstellung von Markasit, Pyrit, und Magnetkies aus wässrigen Lösungen bei Zimmertemperatur: Heidelberger Beiträge zur Min. und Pet., v. 5, p. 146–164.
7. Skinner, B. J., 1958, The geology and metamorphism of the Nairne pyritic formation: ECON. GEOL., v. 53, p. 546–562.

Economic Geology
Vol. 54, 1959, pp. 336–339

REVIEWS

Spravochnoe rukovodstvo po petrografii osadochnykh porod. [A reference manual on the petrography of the sedimentary rocks.] Edited by V. B. TATARSKII AND L. B. RUKHIN. In two volumes, 70 × 108 cm.; pp. 486 + 520; pl 32. Gostoptekhizdat, Leningrad, 1958. Price, 50r. (Russian only.)

Although professedly prepared for use mainly in the petroleum and coal industries, this lengthy compilation by 29 different authors contains much information on the sedimentary rocks which is of widespread application in other aspects of economic geology, and the aim of the authors to produce a reference work rather than a text-book has resulted in a most useful publication of a unique kind. The coverage is perhaps best indicated by the chapter headings, which in summary are as follows. Volume I: (1) introductory review; (2) classification; (3) chemical composition; (4) weathering, transport and deposition; (5) lithification; (6) the facies concept; (7) macroscopic structures; (8) physical properties; (9) geophysical methods of study; (10) mineralogy of sediments (224 pp.); (11) mineralogy of rock-forming fossils (46 pp.); (12) the organic components of coals and oil-shales. Volume II: (1) pyroclastic rocks; (2) conglomerates and breccias (62 pp.); (3) sandstones (70 pp.); (4) argillaceous rocks; (5) coal deposits; (6) allitic (i.e., bauxitic) rocks; (7) sedimentary iron ores; (8) sedimentary manganese ores; (9) flint, chert, etc.; (10) phosphorites; (11) carbonate rocks (34 pp.); (12) gypsum and anhydrite; (13) salt deposits; (14 cupriferous sediments; (15) glauconitic rocks; (16) zeolite-bearing sediments; (17) sulphur deposits in sedimentary rocks; (18) bitumens, naphthids and naphthoids; (19) sedimentary borate deposits. Most of these 31 chapters are concerned rather more with general problems of genesis, nomenclature, or classification, than with discussions of already well-documented occurrences. An extensive bibliography on each topic is valuable since the monograph is largely culled from Russian publications that are little known in the West.

C. F. DAVIDSON

UNIVERSITY OF ST. ANDREWS,
SCOTLAND,
Nov. 1, 1958.

Geologicheskii Slovar. (Geological Glossary.) A. N. KRISHTAFOVICH (editor) and others. Vol. 1, pp. 402; Vol. 2, pp. 445. Gosgeoltekhizdat, Moscow, 1955. Circulation 30,000. Price (for both volumes): roubles 53.20. In Russian only.

Diccionario de Geologia y Ciencias Afines. PEDRO DE NOVO Y F. CHICARRO (editor in chief). Vol. I, pp. 797; figs. 39. Vol. II, pp. 798–1685; figs. 1650. Editorial Labor, S. A., Barcelona, 1957. Price (for both volumes) $24.50. In Spanish only.

Another addition to the record of geological glossaries should be made since the review by G. C. Amstutz (ECONOMIC GEOLOGY, 1957, v. 52, pp. 840–842).

The Russian glossary has been prepared by a large group of research associates of the geological institute VSEGEI in Leningrad, and other geological institutions of the Soviet Union. It gives concise and explicit definitions of terms used in general geology, geomorphology, geochemistry, hydrogeology, glaciology, vulcanology, engineering geology, crystallography, lithology, paleontology, petrology, economic geology, exploratory geophysics, stratigraphy, and tectonics. The glossary contains 12,000 terms arranged in alphabetical order. Etymological meanings are indicated. Obsolete names of minerals and stratigraphic terms have not been included. The authors admit that the glossary has certain shortcomings. A review of the work will show that not all terms are included. This is also mentioned by G. V. Tokhtuev (Razvedka i Okhrana Nedr, 1958, n. 6, p. 60). However, it does not greatly change the value of the glossary. It is understandable that no glossary can be really all-inclusive. The first edition is sold out, and a new one is under way. This glossary will be of great help to geologists outside the Soviet Union who possess some knowledge of Russian, and will allow them to benefit from the latest Russian geological publications, as well as to study the vast resources of Russian geological literature which have accumulated since the turn of the century.

The Spanish glossary is the result of the cooperation of a group of prominent Spanish geologists and scholars. Besides an explanation of the meaning of each term, an indication of its origin is given. Translations of some foreign terms (mainly German) are included. Individual definitions contain an adequate amount of information, equal to or exceeding that given in the Glossary of Geology published by the American Geological Institute. The work contains about 25,000 terms, and seems to top in this respect all other geological glossaries published to date. It is an excellent accomplishment and will be of great assistance to professional people dealing with Spanish and Latin American literature. However, it seems that the glossary would have benefited by not being subdivided into separate sections, such as: stratigraphy, orogeny and tectonics, physical geography, mineralogy, paleobotany, etc.

EUGENE A. ALEXANDROV

DEPARTMENT OF GEOLOGY,
COLUMBIA UNIVERSITY,
Dec. 24, 1958

Prospection et protection du sous-sol: A translation of the Russian periodical *Razvedka i okhrana nedr*. Produced by the Bureau de Recherches Géologiques, Géophysiques et Minières, Paris. Monthly. Price 400 francs each issue.

The Russian journal *Razvedka i okhrana nedr* [Mineral exploration and conservation] is a monthly publication of the U.S.S.R.'s Ministry of Geology, concerned principally with the dissemination of information on geological, geochemical and geophysical prospecting methods and on techniques for the evaluation of ore reserves. It is essentially a practical rather than an academic publication, but some of its articles on the results of recent prospecting operations, on proposals for future explorations, on recent publications and on geological conferences within the Soviet Union are of general interest. Under the direction of Professor Laffitte, the B.R.G.G.M. in Paris has undertaken the systematic publication of a translation of each issue, this French edition thus greatly extending the availability of the journal to Western readers. The first six numbers to be translated (January–June, 1958) have all appeared within three months of the Russian versions, a rapidity which has been facilitated by close co-operation with the editorial staff in Moscow. For a

work produced so speedily the standard of the translation is remarkably high. Each issue extends to 64–68 pages, containing upwards of a dozen original articles.

C. F. DAVIDSON

DEPT. OF GEOLOGY,
ST. ANDREWS, SCOTLAND,
Dec. 1, 1958

Geologicheskoe stroenie SSSR. (Geological structure of the U.S.S.R.) Editor-in-chief, A. P. MARKOVSKII. In four volumes. Vol. I, Stratigraphy, 588 pp., 14 folding tables; Vol. II, Magmatism, 332 pp., 7 folding tables; Vol. III, Tectonics, 384 pp., 27 folding maps; Vol. IV (supplement to Vol. I), colored geol. map of U.S.S.R., scale 1:7,500,000, with geomorphological map, 1:15,000,000. Gosgeoltekhizdat, Moscow, 1958. Price 108 roubles. (Russian only.)

To write a brief notice worthy of this immense work by more than 150 authors is beyond the reviewer's powers. Perhaps it need only be said that it is the most useful publication of recent years on the general geology of the Soviet Union. In style, most of the text is highly condensed and factual, devoid of discursive matter; and it is therefore possible for a western reader with but a dictionary knowledge of the Russian language to obtain from it a balanced conspectus of the rock formations of any geological age in any region of the U.S.S.R. The first volume begins with sketches of the geomorphology and geology of the U.S.S.R. as a whole, succeeded by a detailed account of the stratigraphical development system by system, with treatment on a regional basis within each system. A similar procedure is followed in volume II, concerned with igneous geology; and in both of these volumes the many detailed correlation tables incorporated as large folders in the text provide keys to the overall story. More than half of the third (most difficult) volume is concerned with regional tectonics and it closes with a 140-page review of the tectonic development of the U.S.S.R. as a whole. Only very brief references are made to mineral deposits, and there is neither a bibliography nor an index (though the latter is scarcely necessary). The accompanying portfolio (volume IV) contains a 1:7,500,000 geological map in two sheets, well printed in 80 colors.

C. F. DAVIDSON

UNIVERSITY OF ST. ANDREWS,
SCOTLAND,
January 12, 1959

Le Ciel et La Terre. Vol. III. Directors, ANDRÉ DANJON, PIERRE PRUVOST, and JULES BLACHE. Pp. 1½ inches thick. Société Nouvelle de L'Encyclopédie Française, Paris, 1956.

This monumental work appears as a huge volume measuring 10 × 12 inches, and 1½ inches in thickness. To figure the number of pages would require an adding machine and much time since there are 58 sections each paginated separately.

This Volume III of the Sky and the Earth is presented in two parts, the Sky, and the Earth. Under the first part, Section A, the earth and the solar system, treats of the earth and its dimensions, the atmosphere, weather, and the constitution of the solar system. Section B deals with the sun and the stars; Section C, the galaxies; and Section D, the problems of evolution of the solar system.

The second part, the earth, is divided into three sections. The first one reviews the atmosphere, the ionosphere, terrestrial magnetism, gravity and istostacy, physics of the interior, and seismology. Section B relates to the earth's crust—the evolution of the crust, the formation of its materials, sedimentation, volcanism, metamorphism, and geologic history.

Section C is largely geomorphology and physical geology, dealing with the atmosphere and climate and their geologic role; surface and underground waters; rivers and their work, earth forms; and submarine relief.

The volume is abundantly illustrated and also contains colored paleographic maps of Europe and a colored map showing the broader geologic and tectonic outlines of the world. The work represents contributions from some four dozen authors, mostly French. The book is made up in loose-leaf form, so that additional pages may be added later.

It is an excellent though ungainly reference covering the many subjects treated.

The Geology of South Australia. Edited by M. F. GLAESSNER and L. W. PARKIN. Pp. 163; figs. 26; pls. 11; maps 6. Melbourne University Press, Melbourne, 1958. Price, $8.50.

This authoritative volume has been compiled by M. F. Glaessner of the University of Adelaide, and L. W. Parkin of the Geological Survey of South Australia. It contains the contributions of eleven members of the South Australian Division of the Geological Society of Australia.

The arrangement of the book is rather unique, in that it has departed from the normal practice of stratigraphic divisions, discussed in historical order. Instead, a chapter is devoted to each of the ten natural geologic provinces, which can be confusing to the stranger unfamiliar with the areas concerned. However, chapter 11 contains a summary of tectonics and sedimentation that is clearly and efficiently written; the reader would do well to study this chapter before considering the details of the several geologic provinces. Of particular interest are the petrological features of the Precambrian shield areas, the stratigraphy and structure of the folded zones, and the subsurface stratigraphy and correlation in the great basins, which are largely covered by young deposits.

The geologic maps are generalized to the extent that the reader is not confused by a mass of detail, but instead receives an accurate view of the structure generally. They are lacking somewhat in that not all the places mentioned in the text are to be found on the maps. A number of the photographs are very striking, especially the areal views of the sweeping folds of the Willouran Ranges. At the end of each chapter brief reference is made to economic resources. For the sake of those interested in economic geology, it is regretted that the resources could not have been covered in more detail.

In general, however, for those who desire to learn more of the geology of Australia, this volume will make interesting reading, as well as an invaluable reference book.

R. F. LAGANZA

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February 3, 1959

BOOKS RECEIVED

JAMES M. ALLEN AND JOHN W. SALISBURY

Radioactive Measuring Instruments, by M. C. NOKES. Pp. 75; figs. 38. Philosophical Library, New York, 1958. Price, $4.75. *Underlying principles, descriptions, and use of Geiger counters, trigger devices, power, ratemeters and scalers, and practical hints of how to build and make them.*

Problèms de Géologie Sous-Marine, by JAQUES BOUCART. Pp. 128; figs. 20. Évolution des Sciences No. 12. Masson et Cie., Editeurs, Paris, 1958. Price (paper cover), 980 francs. *This book deals with various submarine problems—the precontinent, the littoral and its preservation, and submarine stratigraphy.*

Economics for the Mineral Engineer, by EDMUND J. PRYOR. Pp. 254; figs. 14. Pergamon Press, New York, 1958. Price, $6.00. *Economics of mineral engineering for the miner, metallurgist, plant superintendant, and executives; prospecting and sampling, accounts, management, mill records, plants, marketing, and an excellent glossary.*

Dictionary of Astronomy and Astronautics, by ARMAND SPITZ and FRANK GAYNOR. Pp. 439. Philosophical Library, New York, 1959. Price, $6.00. *Concise definitions of 2,200 terms and concepts related to astronomy and astronautics —an indispensable dictionary.*

Minerals Yearbook 1957. Vol. I. Metals and Minerals (Except Fuels). STAFF OF THE BUREAU OF MINES. Pp. 1367. U. S. Govt. Printing Office, Washington, 1958. *Includes chapters on metal and non-metal mineral commodities, with the exception of mineral fuels. Included also are a chapter reviewing these mineral industries, a statistical summary, and chapters on mining technology, metallurgical technology, and employment and injuries.*

National Science Foundation 8th Annual Report 1958. Pp. 246; pls. 8; figs. 5; tbls. 5. Price, $1.00. U. S. Govt. Printing Office, Washington, 1959. *Summary of research projects supported by the Foundation.*

Annual Report of the Director of the Geophysical Laboratory 1957–1958. Pp. 260; pls. 2; figs. 48; tbls. 7. Reprinted from *Carnegie Institution of Washington Year Book 57*, Washington, 1958. *Summary of experimental results for work in progress at the Laboratory.*

Journals and Serial Publications from the U.S.S.R., Poland, Rumania, Czechoslovakia, Bulgaria, Hungary and Yugoslavia. (List No. 1630, Code Word: SCIALL.) Pp. 23. Davies Book Co., Ltd., 3468 Melrose, Montreal, Canada. *An extensive bibliography of books and publications on pure and applied sciences which are available from the Davies Book Co. Supplied on request to any library.*

Structures of Molecular Complexes Found in Heavy Petroleum Fractions. G. W. LEMAIRE. Pp. 79; figs. 44; tbl. 1. Price, $1.50. Quarterly of the Colorado School of Mines, Vol. 53, No. 4, Golden, 1958. *Review of investigations and additional research done on the heavier hydrocarbons in natural crude oils.*

Proposition d'une règle de répartition zonale des concentrations d'uranium par rapport aux plutons. P. ROUTHIER and J.-P. GAUTSCH. Pp. 4. Reprinted from Comptes rendus des séances de l'Académie des Sciences, t. 247, pp. 1750–1753. Paris, 1958.

Geologie, Jahrgang 7, Heft 3–6. Pp. 237–860; pls. 45; figs. 103; tbls. 7. Akademie-Verlag, Berlin, 1958. *Forty-three articles on structural, metamorphic, petrologic, economic, stratigraphic, and paleontologic subjects.*

Summary of Progress of the Geological Survey of Great Britain and the Museum of Practical Geology for the Year 1957. Pp. 65. Price, 5 sh. Geological Survey of Great Britain, London, 1958. *Report of activities of the survey during 1957 in England, Wales, Scotland and Northern Ireland.*

Variations in Isotopic Abundances of Strontium, Calcium, and Argon and Related Topics. M.I.T. STAFF, VISITORS, and STUDENTS. Pp. 193; figs. 14; tbls. 31. Dept. of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge, 1958. (NYO-3939. Sixth Annual Progress Report for 1958, U. S. Atomic Energy Commission Contract AT30-1-1381.) *Progress report on work completed since the previous report nine months ago.*

Geology of the Hanover Quadrangle, New Hampshire. J. B. LYONS. Pp. 43; figs. 9. The New Hampshire State Planning and Development Commission, Concord, 1958. *Physical geology, structure, glacial and economic geology, points of interest.*

An Outline Survey of India's Economic Minerals. B. RAMA RAO. Pp. 62; pl. 1; fig. 1. Sri Rama Press, Bangalore, 1958. *Semi-technical pocket booklet giving concise account of India's useful minerals.*

Manganese as a Factor in Indo-American Relations. M. S. VENKATARAMANI. Pp. 23; tbls. 5. India Quarterly, Vol. XIV, No. 2, New Delhi, 1958. *The role of manganese is discussed from political, military, and economic points of view It is significant that Brazil replaced India as the principal supplier of manganese to the United States in 1957.*

Records of the Geological Survey for the Year Ending 31st December, 1956. Pp. 58; pls. 9; tbls. 5. Price, 5 s. Northern Rhodesia Geological Survey, Lusaka, 1958. *Preliminary reports on areas and subjects under investigation.*

Annual Report of the Geological Survey Department—Somaliland. Pp. 18; Price, 2 sh. Somaliland Protectorate, Hargeisa, 1958. *Activities of the survey for the period April 1957–March 1958.*

Oil Development and Production in India During 1956. T. A. DAWSON and G. L. CARPENTER. Pp. 12; fig. 1; tbls. 2. Indiana Geological Survey, Mineral Economics Series Nos. 3 and 4, Bloomington, 1958. *Production figures listed by field. Oil production in 1957 increased 33,000 bbl. over the 11,777,000 bbl. produced during 1956.*

Eleventh Biennial Report, State of Oregon, 1956–1958. Pp. 40; figs. 16; tbls. 4. Oregon Department of Geology and Mineral Industries, Bull. 48, Portland, 1958. *Summary of the Department's projects and services, and Oregon's mineral industry.*

Mineral Production in South Dakota in 1955 and 1957. Pp. 26; figs. 4; tbls. 13. South Dakota Geological Survey Minerals Reports 1 and 2, Vermillion, 1958. *Mineral production statistics for 1954 through 1957.*

Annual Report of the Geological Survey Dept. Tanganyika—1957. Pp. 18. Geologic map, 1:125,000. Dar es Salaam, 1958. *Report of activities for 1957.* **Technical Reports No. 2.** Pp. 175; pls. 34. Price, 5/–. Tasmania Department of Mines, Hobart, 1957. *Articles on mineral deposits, engineering geology, mining, and ore dressing in Tasmania.*

A Comparative Study of Statistical Analysis and Other Methods of Computing Ore Reserves, Utilizing Analytical Data from Maggie Canyon Manganese Deposit, Artillery Mountains Region, Mohave County, Arizona. S. W. HAZEN, JR. Pp. 135; figs. 33; tbls. 29. Price, $1.00. U. S. Dept. of Interior,

Rept. of Invest. 5375, Washington, 1958. *Application of statistical methods to tonnage and grade estimation. Review of previous literature.*

Service de la Carte Géologique de l'Algérie—Alger, 1957–1958.

Bull. 13. Travaux des Collaborateurs 1956. Pp. 281; pls. 15; figs. 35. *Various papers on stratigraphy, paleontology, petrology and general geology. In French.*

Bull. 15. Sables Quaternaires du Sahara Nord-Occidental (Saoura-Ougarta). MARIE-HENRIETTE ALIMEN. Pp. 207; pls. 8; figs. 89. *Distribution and character of sands of the western Sahara. In French.*

Bull. 18. Les Formations Volcaniques Tertiaires et Quaternaires du Tell Oranais. GÉRARD SADRAN. Pp. 533; pls. 51; figs. 61. *General geology, structure and petrology of region in N.W. Algeria underlain by Tertiary and Quaternary volcanics. In French.*

Évaluation des Perspectives Économiques de la Recherche Minière sur de Grands Espaces. M. ALLAIS. Pp. 101; figs. 16; tbls. 25. *Statistical approach to evaluation of ore deposits. In French.*

Bureau of Mineral Resources, Geology and Geophysics—Melbourne, Australia, 1957–1958.

The Australian Mineral Industry—Quarterly Review and Quarterly Statistics. Vol. 11, No. 2. Pp. 18; figs. 2; tbls. 11. Price, 3/–. *Quarterly review of the mineral industry from aluminum to zirconium, with statistics on production and import-export.*

The Australian Mineral Industry 1957 Review. Pp. 242. Price, 12/–. *Statistics of production and utilization of minerals in Australia during 1957.*

Rept. 41. Summary of Oil-Search Activities in Australia and New Guinea to the End of 1957. M. A. CONDON, N. H. FISHER, and G. R. J. TERPSTRA. Pp. 98; pls. 12; tbls. 9. *Summary of geological and geophysical works, drilling done in Australia and the Australian territories.*

Bull. 39. The Permian Orthotetacea of Western Australia. G. A. THOMAS. Pp. 111; pls. 20; figs. 11; tbls. 17. *Distribution, types of orthotetacea in Western Australia.*

California Department of Natural Resources, Division of Mines—San Francisco, 1958.

Spec. Rept. 50. Plants as a Guide to Mineralization. D. CARLISLE and G. B. CLEVELAND. Pp. 31; figs. 10. Price, 50 cents. *Theoretical and practical discussion of biogeochemical prospecting with several field studies for molybdenum. Extensive bibliography.*

Vol. 54, No. 2. California Journal of Mines and Geology. Pp. 501–602; pl. 1; figs. 10; tbls. 20. *Two articles entitled Mines and Mineral Resources of Contra Costa County, California, and Research in Mining and the Mineral Industries in California. Also contains the index to Vol. 54. Available Publications.* M. H. RICE and E. L. EGENHOFF. Pp. 27; figs. 3. Supplement to Mineral Information Service, Vol. 11, No. 11. *Geologic Map of California, Death Valley Sheet. Price, $1.50. Scale, 1:250,000.*

Freiberger Forschungshefte—Berlin, 1958.

C 45. Geophysik. Pp. 99; figs. 20. *Various geophysical papers. In German.*

C 48. Methoden der Geomikrobiologie. W. SCHWARTZ and ADELHEID MÜLLER.

Pp. 39; figs. 19. *Discussion of the role of organisms in some geologic processes. In German.*

C 54. Lagerstättenkunde. Pp. 128; tbls. 10. *A classification of mineral reserves. In German.*

Illinois Geological Survey—Urbana, 1958.

Circ. 260. Strippable Coal Reserves of Illinois. Pt. 2. Jackson, Monroe, Perry, Randolph, and St. Clair Counties. W. H. SMITH. Pp. 35; pls. 4; figs. 4; tbls. 6. *Coal in beds at least 18 inches thick and covered by not more than 150 feet of overburden is estimated at 3 billion tons.*

Circ. 261. Some Plastic Properties of Pastes Made from Hydrated Dolomitic and High-Calcium Limes. D. L. DEADMORE and J. S. MACHIN. Pp. 9; pls. 2; figs. 3; tbls. 7.

Circ. 262. Studies of Waterflood Performance. IV. Influence of Curtailments on Recovery. W. ROSE. Pp. 32; figs. 8; tbl. 1. *Examples are cited which show that high rates of recovery are advantageous in some cases and not in others.*

Bull. 85. Petroleum Industry in Illinois in 1957. Pt. I. Oil and Gas Developments. Pt. II. Waterflood Operations. A. H. BELL, VIRGINIA KLINE, and C. W. SHERMAN. Pp. 115; figs. 8; tbls. 15.

Reprint Series 1959B. Six Case Histories of Resistivity Prospecting in Illinois. M. B. BUHLE. Pp. 205–213; figs. 6. *Reports successful applications to the detection and study of deposits of water-bearing sand and gravel occurring within the glacial till covering a large portion of the state.*

Geological Survey of Japan—Hisamoto-chō, Kawasaki-shi, 1958.

Explanatory Text of the Geological Map of Japan. Kakinoura (Fukuoka-79). H. NAGAHAMA and K. MATSUI. Pp. 72; pls. 10; figs. 15; tbls. 2. *Physical geology of a region in northwestern Kyushu underlain by metamorphic rocks, granite Tertiary sediments, and lavas. Coal is the only economic product. In Japanese; English summary. Map, scale 1:50,000.*

Explanatory Text of the Geological Map of Japan. Agematsu (Kanazawa-73). M. KATADA and H. ISOMI. Pp. 46; figs. 17; tbls. 2. *Physical geology of terrain underlain primarily by volcanic and igneous rocks of Mesozoic and Tertiary age. Map, scale 1:50,000. In Japanese, English summary.*

Kansas Geological Survey—Lawrence, 1958.

Bull. 130, Pt. 5. History of Cretaceous Structural Studies in Kansas. D. F. MERRIAM. Pp. 14; figs. 6. *Discussion of 5 structural maps of the top of the Dakota sandstone prepared over the period 1905 to 1957.*

Bull. 130, Pt. 6. The Mineral Industry in Kansas in 1957. W. H. SCHOEWE. Pp. 193–242; figs. 3; tbls. 18. *Production and value of all minerals produced in the state in 1957 and comparison with 1956. Includes directory of mineral producers on record as of December 31, 1957.*

Missouri Geological Survey—Rolla, 1958.

Rept. of Investigations 24. Resistivity Surveys of Missouri Limonite Deposits. T. MEIDAV, W. C. HAYES and G. E. HEIM. Pp. 27; figs. 16; tbls. 4. *Description of electrical method for outlining limonite deposits in sinkhole-like depressions.*

Publications of Division of Geological Survey and Water Resources. Pp. 25.

Montana Bureau of Mines and Geology—Butte, 1958.

Information Circ. 26. A Summary Report on the Ground-Water Situation in Montana. S. L. GROFF. Pp. 45; pls. 7; tbl. 1. *Presents basic concepts of ground-water science and general summary of ground-water conditions in eastern, central and western Montana. Contains chapter by A. W. Stone on Montana law on groundwater.*

Biennial Report of the Montana Bureau of Mines and Geology 1956–1958. Pp. 57; figs. 2; tbls. 2. *Describes status of projects undertaken by the different divisions of the Bureau and includes appendices showing mineral production and rank of minerals produced in Montana, 1956 and 1957.*

New Zealand Geological Survey—Wellington, 1958.

Bull. n.s. 58. The Geology of the Eglinton Valley, Southland. G. W. GRINDLEY. Pp. 68; pls. 3; figs. 27; tbls. 8. Price, 20 s. *Areal report. Geologic map, scale 1: 253,440.*

Bull. n.s. 60. Regional Metamorphism in South-East Nelson. J. J. REED. Pp. 64; pls. 5; figs. 33; tbls. 17. Price, 12 s. *Regional metamorphism is mapped over an area of 500 square miles, and three metamorphic zones are recognized.*

Ontario Department of Mines—Toronto, 1958.

Map No. 1958A. Map of the Province of Ontario Showing Geological Maps Published by the Ontario Dept. of Mines 1891–1958.

Aeromagnetic Map, Township of Goschen, District of Sudbury.

Aeromagnetic Map, Township of Stalin, District of Sudbury.

Aeromagnetic Map, Township of Whitefish Lake Indian Reserve No. 6, District of Sudbury.

Aeromagnetic Map, Township of Sale, District of Sudbury.

Aeromagnetic Map, Township of Louise and Part of Whitefish Lake Indian Reserve No. 6, District of Sudbury.

Aeromagnetic Map, Township of Eden and Part of Whitefish Lake Indian Reserve No. 6, District of Sudbury.

Aeromagnetic Map, Township of Caen and Part of Whitefish Lake Indian Reserve No. 6, District of Sudbury.

Aeromagnetic Map, Township of Bevin, District of Sudbury.

Aeromagnetic Map, Township of Dieppe, District of Sudbury.

Geological Circ. 7. Offshore Exploration for Gas Under the Canadian Waters of the Great Lakes. A. C. NEWTON. Pp. 28; figs. 11; pl. 2. *An account of oil and gas drilling operations in Lake Erie and Lake St. Clair.*

Sixty-Sixth Annual Report.—Vol. LXVI, Pt. 2, 1957. Mining Operations in 1956. D. J. FIELD. Pp. 161. *Review of mining operations in Ontario during 1956.*

Fourth Annual Report of the Ontario Fuel Board 1957. Pp. 164; pls. 2; figs. 4; tbls. 21. *A continuation of Part III of the Annual Report of the Ontario Department of Mines with chapters on exploration, drilling and production of natural gas and petroleum.*

Canadian Department of Mines and Technical Surveys—Ottawa, 1958.

No. 855. The Industrial Minerals of Newfoundland. G. F. CARR. Pp. 158; pls. 33; figs. 9; tbls. 12. Price, $2.00. *Industrial mineral production to 1956, with brief descriptions of mines and prospects.*

Eighth Annual Report of the National Advisory Committee on Research in the Geological Sciences, 1957–1958. Pp. 165; pl. 1. Price, 50 cents. *Summary of the activities of the Survey plus a report on current research in the geological sciences in all of Canada.*

Pennsylvania Geological Survey—Harrisburg, 1958.

Well-Sample Record 39. Goodwill-Curley No. 1 Well, Summit Township, Erie County. W. R. WAGNER. Pp. 48. *Includes a skeletal log of the samples and a detailed sample description. Well obtained 100 M.C.F. gas at 3447 feet from the Whirlpool.*

Well-Sample Record 40. Emma McKnight No. 1 Well, Pymatuning Township, Mercer County. W. R. WAGNER. Pp. 36. *Sample descriptions from dry hole penetrating 8210 feet of section.*

Progress Rept. 154. Oil and Gas Developments in Pennsylvania in 1957. W. S. LYTLE, J. M. BERGSTEN, A. S. CATE, and W. R. WAGNER. Pp. 46; figs. 5; tbls. 7. *New developments in the petroleum industry.*

Geologic Atlas of Pennsylvania 167C. Geology of the Lebanon Quadrangle. A. R. GEYER, C. GRAY, D. B. MCLAUGHLIN, and J. R. MOSELEY. *General Geology of the area in S.E. Pennsylvania.*

Quebec Department of Mines—1958.

Geological Rept. 78. Bourget Area. RENÉ-F. JOOSTE. Pp. 40; maps 2; pls. 12; tbls. 2. *Geology of a largely igneous terrain in southeastern Quebec. Titaniferous magnetite deposits occurring in the area are described.*

Geological Rept. 81. Rinfret Area. W. W. LONGLEY. Pp. 20; pls. 12; map, scale 1:63,360. *Areal geology of igneous and metamorphic terrain immediately east of Chibougamau in north-central Quebec.*

Tennessee Department of Conservation—Nashville, 1958.

Information Circ. 6. The Zinc Industry of Tennessee. S. W. MAHER. Pp. 28; figs. 3. *History of production, geology, mining, milling, and marketing of zinc in Tennessee.*

Rept. of Investigations 8. Structure of the Cumberland Plateau, Tennessee. C. W. WILSON, JR., and R. G. STEARNS. Pp. 14; figs. 8. Reprinted from Bull. of Geological Soc. of America, Vol. 69, pp. 1283–1296, October, 1958. *Confirms the low-angle, "no basement" thrusting previously attributed to the Plateau.*

Bureau of Economic Geology, The University of Texas—Austin, 1958.

Rept. of Investigations 36. Tertiary Formations of Rim Rock Country, Presidio County, Trans-Pecos Texas. R. K. DEFORD. Pp. 37; figs. 4. *Stratigraphy of Tertiary tuffs and sediments in south-west Texas.*

Rept. of Investigations 37. Mineral Resources of the Colorado River Industrial Development Association Area. J. W. DIETRICH and J. T. LONSDALE. Pp. 81; figs. 22; pls. 9; tbls. 9. *Economic potentialities of a 10-county region on the lower watershed of the Colorado. Industrial rocks and minerals are of greatest importance.*

Guidebook No. 1. Field Excursion Ealster Llano Region. V. E. BARNES. Pp. 36; figs. 12. *Guidebook for field excursion into the Llano Region.*

State of Washington Geological Survey—Olympia, 1958.

Biennial Rept. 7 of the Division of Mines and Geology. M. T. HUNTTING. Pp. 19; fig. 1; tbl. 1. *Report on the activities of the Division, including mining and milling statistics, for the period commencing July 1, 1956 and ending June 30, 1958.*

Information Circ. 30. Archeology in Washington. BRUCE STALLARD. Pp. 65; pl. 1; figs. 34. Price, 50 cents. *Both a general survey of archeology in Washington with a bibliography of more specific literature, and an explanation and introduction to the science of archeology for those not yet acquainted with the subject.*

West Virginia Geological Survey—Morgantown, 1958.

Bull. 14. Ground-Water Resources of Harrison County, West Virginia. R. L. NACE and P. P. BIEBER. Pp. 42; pl. 1; figs. 1, tbls. 11. *Types, analyses of water available and factors affecting supply.*

Map of Wirt, Roane and Calhoun Counties Showing Oil and Gas Fields. Geologic map, scale 1:62,500. *Map showing oil and gas fields and structure contours on the top of the Greenbriar limestone.*

U. S. Geological Survey—Washington, D. C., 1958.

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Bull. 1046-O. Reconnaissance for Radioactivity in the Metal-Mining Districts of the San Juan Mountains, Colorado. C. T. PIERSON, W. F. WEEKS, and F. J. KLEINHAMPL. Pp. 385–413; pls. 2; figs. 3; tbls. 4. *Thirty-four mining districts were tested for radioactivity. Although anomalous radioactivity was*

found in fifteen of the districts, none of the deposits at sample localities can be classed as commercial. Additional prospecting might result in the discovery of small ore deposits of uranium.

Bull. 1053. Geology and Coal Resources of the Centralia-Chehalis District, Washington. P. D. SNAVELY, JR., R. D. BROWN, JR., A. E. ROBERTS, W. RAU, and J. M. SCHOPF. Pp. 157; pls. 13; figs. 25; tbls. 2. *Structure, stratigraphy of coal-bearing Tertiary rocks in central Washington. Reserves of 3½ billion tons of subbituminous C rank coal.*

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Bull. 1061-E. Vegetation of Northwestern North America, as an Aid in Interpretation of Geologic Data. R. S. SIGAFOOS. Pp. 165–185; pls. 5; figs. 2. Price, 75 cents. *A distribution map of the major forest groups of northwestern North America and some treeless vegetation types of parts of Alaska. Map, scale 1:2,500,000.*

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Bull. 1070B. Lead-Alpha Ages of the Mesozoic Batholiths of Western North America. E. S. LARSEN, JR., D. GOTTFRIED, H. W. JAFFE, and C. L. WARING. Pp. 26; figs. 2; tbls. 12. Price, 15 cents. *Similar ages are recorded for: the Baja and Southern California, the Sierra Nevada, Idaho, and Coast Range batholiths. On other grounds these batholiths are considered to be Late Cretaceous, Late Jurassic, Cretaceous and Late Jurassic in age, respectively.*

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Bull. 1086-C. Geophysical Abstracts 174 July–September 1958. D. B. VITALIANO, S. T. VESSELOWSKY, and others. Pp. 207–326. Price, 35 cents.

Prof. Paper 305-E. Test Well Grandstand Area Alaska. F. M. ROBINSON. Pp. 317–339; pls. 2; figs. 5. *Includes stratigraphic, paleontologic, logistic, and*

engineering data obtained in the drilling of a dry hole. Micropaleontology by H. R. Bergquist.

Prof. Paper 305-F. Test Wells, Meade and Kaolak Areas, Alaska. F. R. COLLINS. Pp. 341–376. Pls. 4; figs. 5. *Lithologic, paleontologic, logistic, and engineering information obtained in drilling two dry holes. Micropaleontology by H. R. Bergquist.*

Prof. Paper 314-D. Geochemistry of Uranium in Apatite and Phosphorite. Z. S. ALTSCHULER, R. S. CLARKE, JR., and E. J. YOUNG. Pp. 45–90; pls. 3; figs. 13; tbls. 27. Price, 60 cents. *Apatite contains only traces of uranium, yet as apatite is a minor constituent in most rocks and the major constituent on a few very large deposits, it accounts, paradoxically, for both dispersal and concentration of a very large percentage of uranium in nature.*

Prof. Paper 316-B. Interpretation of an Aeromagnetic Survey of Indiana. J. R. HENDERSON, JR. and I. ZEITZ. Pp. 18; pls. 2; figs. 10. Price, 75 cents. *Aeromagnetic survey results correlated with gravity and seismic surveys, and well logs to prepare a contour map of the Precambrian surface.*

Water-Supply Paper 1429. Reconnaissance of the Geology and Ground Water of the Khorat Plateau, Thailand. P. E. LAMOREAUX, J. CHARALJAVANAPHET, and others. Pp. 62; pls. 9; figs. 11; tbls. 2. *Reconnaissance made with special reference to the development of supplies of ground water for public and domestic use and the location of potential resources of water for proposed industrial and irrigation use.*

Water-Supply Paper 1462. Geology and Ground-Water Features of Scott Valley Siskiyou County, California. S. MACK. Pp. 98; pls. 7; figs. 17; tbls. 12. *Surface water and ground water in the area are of low mineral content, and are generally of excellent quality for most uses.*

Economic Geology
Vol. 54, 1959, pp. 349-350

SCIENTIFIC NOTES AND NEWS

The U. S. Government and the State of Pennsylvania will spend $700,000 to protect 50 million tons of anthracite against flooding by the installation of 3 turbine pumps of 500 gpm in the abandoned Stanton mine.

The California Dept. of Natural Resources has published in color the first sheet of twenty of the Olaf P. Jenkins new geologic map of the State. It is the "Death Valley Sheet", covering 2° long. and 1° lat. on a scale of 1:250,000, and measures 37 × 21 inches. It carries a sheet containing a chart of source materials, table of stratigraphic nomenclature and an index map showing U.S.G.S. topographic sheets.

The *American Journal of Science* announces the establishment of a *Radiocarbon Supplement* to be devoted to publication of radiocarbon date lists from world laboratories. Professors RICHARD FOSTER FLINT and EDWARD S. DEEVEY, JR. are the editors. The office of the *Supplement* is the same as that of the *American Journal of Science:* Box 1905A, Yale Station, New Haven, Conn., U.S.A. Volume 1 of the *Supplement* will be separate from the *American Journal of Science* and will be sent to a separate subscription list; Volume 1 is priced at $2.50.

LEWIS G. WEEKS, consulting geologist, Westport, Conn., became the 43rd president of the American Association of Petroleum Geologists on March 19. Serving with him on the 1959–60 Executive Committee of the organization will be GEORGE S. BUCHANAN, HAROLD T. MORLEY, ALFRED H. BELL and editor, GROVER E. MURRAY.

The Society of Economic Paleontologists and Mineralogists has elected to honorary membership HENRYK B. STENZEL, consultant for Shell Development Company, Houston, Tex.

CHARLES CAMSELL died in Ottawa on Dec. 19, 1958, aged eighty-two.

GEORGE VIBERT DOUGLAS, Carnegie Professor of Geology at Dalhousie University, Halifax, from 1932 until 1957, died suddenly at his home in Toronto early in October at the age of sixty-six.

REGINALD EDWIN HORE, well known consulting geologist, of Oakville, Ontario, died recently at his home at the age of seventy-seven.

REGINALD HENRY MINET ANSON-CARTWRIGHT, well known as one of Canada's best known prospectors, died in Toronto in mid-November at the age of seventy-seven.

ROBERT G. DOYLE, formerly associated with the St. Joseph Lead Co. in Missouri as mine geologist, was recently appointed to the position of geologist with the Maine Geological Survey.

O. T. HANSON of Boise, Idaho, has been appointed Idaho state mine inspector, succeeding George McDowell who resigned.

ROBERT B. HOY is assistant to the chairman of the Earth Sciences Department of the Stanford Research Institute, Menlo Park, California. Prior to this Mr. Hoy was chief geologist for the New Jersey Zinc Co.

JOHN R. BOGERT, former chief geologist for the National Lead Co. in Argentina, is now chief geologist for Mining, Management and Manufacturing, Inc. of Flemington, N. J.

H. J. FRASER, president of Falconridge Nickel Mines, Ltd. has been elected to succeed D. BARRINGTON as president and managing director of Ventures Ltd.

A group of four geologists, representing Chile, Ghana, and the Philippines, have arrived in Washington, D. C., to participate in a seven-month photogeological survey, sponsored by the State Department.

DONALD H. MCLAUGHLIN, president, Homestake Mining Company, San Francisco, Calif., has been elected to membership on the Board of Trustees of the Committee for Economic Development.

SIR HAROLD JEFFREYS, Cambridge University, England, will be a visiting lecturer at the School of Mines and Metallurgy and the Department of Mechanics and Materials of the University of Minnesota from April 1 to June 15, 1959.

THOMAS L. WRIGHT, geologist for Aluminum Co. of America, will be exploring for deposits of bauxite near Moengo, Dutch Guiana, with Alcoa's Suriname subsidiary, Suralco.

ROBERT G. DOYLE was recently appointed geologist with the Maine Geological Survey. For five years prior to this he had been associated with St. Joseph Lead Co. in Missouri.

BRUCE E. RUSSELL, geological engineer, has jointed E. J. Longyear Co., Grants, N. M., to do exploration work on San Mateo Dome, N. M. Previously he was with Exploration Services in Denver.

EVAN JUST, formerly vice president of Cyprus Mines Corp., is now president of International Drilling and Water Co. Inc. in New York. He is available for geological and exploration consultation.

RICHARD C. ELY has become a geologist and engineer for Ely and French, geologists.

C. O. MITTENDORF has accepted a position as director of industry and transportation for the International Cooperation Administration's mission to Iran. He has resigned his post as administrator of the Office of Minerals Exploration with the Dept. of the Interior.

L. C. BONHAM has been appointed Supervising Research Geologist in Exploration Research at California Research Corporation's La Habra Laboratory in which position he will supervise a broad program of geology. He joined the company as a research geologist in 1950.

CHARLES L. CHRIST, physicist with the U. S. Geological Survey, has been selected for a Rockefeller Public Service Award for 1959. Presentation will be made at a luncheon in Washington on April 14.

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